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Source-specific biomarkers as proxies for Arctic and Antarctic sea ice

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Abstract: Over the last decade or so, certain source-specific C25 highly branched isoprenoid (HBI) lipid biomarkers have emerged as useful proxies for Arctic and Antarctic sea ice. Thus, IP25 (Ice proxy with 25 carbon atoms) and IPSO25 (Ice proxy for the Southern Ocean with 25 carbon atoms) represent binary measures of past seasonal sea ice in the Arctic and Antarctic, respectively. A further tri-unsaturated HBI (generally referred to as HBI III) appears to provide proxy evidence for the region of open water found adjacent to sea ice (i.e. the marginal ice zone (MIZ)) in both polar regions. This review provides an update on current knowledge pertaining to each proxy. The first section focuses on describing those studies that have aimed to establish the underlying features of each proxy, including source identification and spatial distribution characteristics. The second section presents some important analytical considerations pertinent to the accurate identification and quantification of HBI biomarkers. The third section describes how each HBI proxy is normally interpreted within the sedimentary record for palaeo sea ice reconstruction purposes. This includes the interpretation of individual and combined biomarker profiles such as the PIP25 index and multivariate decision tree models. A summary of all previous palaeo sea ice reconstructions based on HBIs is also given, which includes examples that clarify or reinforce our understanding of the individual or combined biomarker signatures. Some knowledge gaps and areas for future research are also briefly described.

Highlights (for review)

- Source-specific highly branched isoprenoid (HBI) biomarkers as sea ice proxies
- IP_{25} and $IPSO_{25}$ are proxies for Arctic and Antarctic sea ice, respectively
- A tri-unsaturated HBI shows promise as a proxy for the Marginal Ice Zone (MIZ)
- Combined biomarker approaches provide more detailed sea ice descriptions
- Overview of how HBI-based proxies are used for palaeo sea ice reconstructions

Source-specific biomarkers as proxies for Arctic and Antarctic sea ice.

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Abstract

Over the last decade or so, certain source-specific C_{25} highly branched isoprenoid (HBI) lipid biomarkers have emerged as useful proxies for Arctic and Antarctic sea ice. Thus, IP_{25} (Ice proxy with 25 carbon atoms) and $IPSO_{25}$ (Ice proxy for the Southern Ocean with 25 carbon atoms) represent binary measures of past seasonal sea ice in the Arctic and Antarctic, respectively. A further tri-unsaturated HBI (generally referred to as HBI III) appears to provide proxy evidence for the region of open water found adjacent to sea ice (i.e. the marginal ice zone (MIZ)) in both polar regions. This review provides an update on current knowledge pertaining to each proxy. The first section focuses on describing those studies that have aimed to establish the underlying features of each proxy, including source identification and spatial distribution characteristics. The second section presents some important analytical considerations pertinent to the accurate identification and quantification of HBI biomarkers. The third section describes how each HBI proxy is normally interpreted within the sedimentary record for palaeo sea ice reconstruction purposes. This includes the interpretation of individual and combined biomarker profiles such as the PIP_{25} index and multivariate decision tree models. A summary of all previous palaeo sea ice reconstructions based on HBIs is also given, which includes examples that clarify or reinforce our understanding of the individual or combined biomarker signatures. Some knowledge gaps and areas for future research are also briefly described.

1. Introduction

1.1 Background to sea ice and sea ice proxies

Dramatic changes to climate in the Arctic and Antarctic, beginning towards the end of the last century and continuing towards modern times, have stimulated a large array of research activity into the causes, consequences and contextualisation of these transformations over the last decade or so (IPCC, 2013). Within the overall climate structure of the polar regions, sea ice plays a central role (Thomas, 2017). For example, due to its high albedo (reflectivity), sea ice acts as a highly efficient regulator of incoming solar radiation to the surface oceans, and it also acts as a physical barrier to gas, heat and moisture exchange between the oceans and atmosphere. During formation and melt, sea ice contributes brines and freshwater, respectively, with important consequences for stratification, bottom-water formation and ventilation, in particular (e.g. Dickson et al., 2007 and references therein). A further impact of ice melting during the spring is nutrient release which, when combined with surface layer stratification and increasing light and temperature, often results in intense open water (pelagic) phytoplankton production, especially in the region defined by the retreating ice edge – the so-called marginal ice zone (MIZ) (Smith and Nelson 1986; Smith, 1987; Sakshaug et al., 2009; Perette et al., 2011). Such primary production can exceed that of the permanently open ocean and is often enhanced further through the seeding of the water column by microorganisms residing in bottom ice during the winter, which then proliferate prior to the main bloom of the pelagic community (Michel et al., 1993; Lizotte, 2001). A further community of sea ice-associated (sympagic) organisms undergo rapid growth within the host ice matrix itself, normally as light and nutrient availability increase during spring (for an overview, see Arrigo, 2017).

With substantial changes in sea ice extent, particularly in the Arctic, during the last half century or so (Stroeve et al., 2012; Fetterer et al., 2016, Serreze et al., 2016; Walsh et al., 2017), one area of recent research focus has centred on aiming to better contextualise these modern changes through reconstruction of longer-term palaeo sea ice conditions. This has been achieved largely (although not exclusively) by analysis of various proxies in marine sedimentary archives. A number of proxies for sea ice exist, and many of their relative merits and applications have already been described elsewhere (e.g. de Vernal et al., 2013 and references therein). Sea ice proxies possessing a biological origin are probably the most common, not least because of the influence that sea ice can have on marine-based ecological systems, as described earlier. Indeed, the identification of certain ice-associated diatoms in polar marine sediments has commonly been used as a proxy measure of sea ice occurrence in the past, especially in the Antarctic (Armand et al., 2017). However, most of these represent species whose growth habitat is more closely associated with the open waters of the MIZ rather than that of sea ice itself (Leventer et al., 2008; Leventer, 2013). In contrast, the strictly sympagic community, arguably a more direct proxy measure of sea ice, is often under-represented in sedimentary records, probably due to their generally lower abundance compared to their pelagic counterparts, together with their often higher susceptibility towards degradation in the water column and in sediments (Leventer, 2013).

1.2 Biomarkers as sea ice proxies

The different ecological habitats of various classes, genera or species of microorganisms in polar marine settings offers the potential to identify unique or source-specific lipids that may serve as suitable biomarker proxies for discrete

oceanographic settings. Within the context of sea ice, such settings may be binary in nature, such as its presence or absence. Alternatively, more nuanced scenarios including different ice types, ice thickness, extent or seasonality might also potentially be deciphered. In practice, the main common algal lipid classes including fatty acids and sterols do not sufficiently satisfy the criterion of source-selectivity to be useful, even for distinguishing sea ice cover from open water conditions. An exception can be found, however, in a further lipid group, commonly referred to as highly branched isoprenoids (HBIs), which are biosynthesised by a relatively small number of diatom genera (Volkman et al., 1994; Belt et al., 2000; Grossi et al., 2004; Sinninghe Damsté et al., 2004; Brown et al., 2014b). Despite the near-ubiquity of HBIs in marine and lacustrine locations worldwide (Rowland and Robson, 1990), the sources and distributions of some HBIs make them good candidates for proxies of Arctic and Antarctic sea ice, and in a range of different sea ice settings. The first of these HBIs – IP_{25} (Ice Proxy with 25 carbon atoms; Belt et al., 2007) – is a mono-unsaturated C_{25} HBI (I; Fig. 1) produced by certain Arctic sympagic diatoms (Brown et al., 2014c), but has thus far not been identified in the Antarctic. The second example is a close structural analogue of IP_{25}, but has an additional double bond in its structure (II; Fig. 1). This di-unsaturated HBI co-occurs with IP_{25} in Arctic sea ice and associated sediments but, unlike IP_{25}, is also present in the Antarctic. A recent study confirmed a sea ice diatom origin for HBI II and the term $IPSO_{25}$ (Ice Proxy for the Southern Ocean with 25 carbon atoms) was given, at least when detected in the Antarctic (Belt et al., 2016). Finally, a third (at least) HBI has been linked with open-water (pelagic) conditions in both the Arctic and the Antarctic (Massé et al., 2011; Collins et al., 2013; Belt et al., 2015; Smik et al., 2016a,b). Although a common constituent of marine settings (Belt et al., 2000), this tri-unsaturated HBI, sometimes

118 referred to as HBI III (III; Fig. 1), is also showing potential as a proxy for the MIZ in
119 both polar regions (Collins et al., 2013; Belt et al., 2015; Smik et al., 2016a,b;
120 Köseoğlu et al., 2018a,b).

121 Studies using HBI-based sea ice proxies for palaeo sea ice reconstruction
122 purposes have largely paralleled those aimed at proxy development (see Tables
123 1,2). The majority of reconstructions carried out thus far span the time interval since
124 the last glacial maximum (LGM) and the Holocene, in particular. However, some
125 recent studies have extended timeframes in the Arctic to recent glacial/interglacial
126 intervals (Stein and Fahl, 2012; Hoff et al., 2016; Stein et al., 2017a; Kremer et al.,
127 2018a,b; Lo et al., 2018), the Mid-Pleistocene Transition (Detlef et al., 2018), the
128 Pliocene and Pliocene/Pleistocene boundary (Stein and Fahl, 2013; Knies et al.,
129 2014; Clotten et al., 2018), and the late Miocene (Stein et al., 2016) (see Table 2 for
130 a summary). In the Antarctic, only one study has investigated HBI sea ice proxies in
131 older (last glacial) sediments (Collins et al., 2013).

132 An earlier review of the use of HBIs as sea ice proxies was published in 2013,
133 with IP_{25} as the focus (Belt and Müller, 2013). The purpose of the current review is to
134 provide an update on research activity carried out on IP_{25}, together with an overview
135 of work carried out on other sea ice related HBIs (mainly $IPSO_{25}$ and HBI III).
136 Throughout, an emphasis is placed on describing the advances in our understanding
137 of how these biomarkers may be used as sea ice proxies, rather than in their
138 application for individual case studies. Nonetheless, some brief illustrations of how
139 these proxies have been used in palaeo sea ice reconstructions are also provided,
140 especially when outcomes from these studies help illustrate the individual proxy
141 signatures of these organic geochemicals. Finally, clarification of current knowledge

should, hopefully, prevent incorrect or mis-leading descriptions and interpretations of HBI-based sea ice proxy research in the future.

2. Source-specific HBI sea ice biomarkers

2.1 IP_{25} – a binary measure of Arctic sea ice

The most frequently studied of the different HBI sea ice biomarkers is IP_{25}, first identified in Arctic sea ice and sediments by Belt et al. (2007). IP_{25} has since been identified in numerous Arctic and subarctic surface sediments and downcore records (Fig. 2a,b; Tables 1,2). In contrast, there have been perhaps surprisingly few studies on IP_{25} in its native sea ice and these are restricted, spatially, to the Canadian Arctic Archipelago and Hudson Bay regions (Fig. 2c; Table 1); however, it is worthwhile highlighting some findings from these investigations. For example, although several authors made early suggestions as to the likely origin(s) of IP_{25} (see Belt and Müller, 2013 for a review), it was not until Brown et al. (2014c) carried out analysis of individual sympagic diatom species that definitive source identifications were made. Three (or four) individual sympagic diatom taxa have been identified as producers of IP_{25} - *Pleurosigma stuxbergii var. rhomboides* (Cleve in Cleve & Grunow) Cleve, *Haslea kjellmanii* (Cleve) Simonsen, *H. crucigeroides* (Hustedt) Simonsen and/or *H. spicula* (Hickie) Lange-Bertalot. Further, Brown et al. (2014c) also showed that, despite their relatively low contributions to sympagic diatom communities (typically ca. 1–5%), these IP_{25} producing species are, nevertheless, common across the Arctic and subarctic regions (Fig. 2c). Consistent with this, IP_{25} has been reported in (to date) more than 500 Arctic/subarctic surface sediment samples (Fig. 2a; Table 1). On the other hand, IP_{25} has not, thus far, been identified in any other diatoms, whether sympagic, pelagic or lacustrine. However, studies

dedicated to identifying IP_{25} producers are still rare and other sources may potentially be identified in the future. In two separate time series analyses of sea ice cores taken from Resolute Passage and the Amundsen Gulf (both in the Canadian Arctic Archipelago (CAA)), temporal production of IP_{25} coincided with the spring sympagic bloom (Fig. 3) (Brown et al. 2011; Belt et al., 2013). As such, many authors have subsequently interpreted the occurrence of IP_{25} in the sedimentary record as proxy evidence of seasonal (spring) sea ice (see Belt and Müller, 2013). Following its production in sea ice during spring, IP_{25} is rapidly released into the surface layer of the water column during ice melt. Indeed, analysis of IP_{25} in the water column during the late spring melting phase has demonstrated the dominance of ice algal organic carbon (OC) input to surface waters at this time (Brown et al., 2016). Thus, a source-to-sink model for IP_{25} might be considered as: production by certain sympagic diatoms in the spring, release to the surface layer as a pulse of ice algal organic carbon during early summer ice melt, and deposition in underlying sediments thereafter. This description seems reasonable for regions experiencing annual cycles of first year sea ice formation in autumn/winter and melt in spring/summer, and is supported further by the identification of higher amounts of IP_{25} in some sediment trap studies during the late spring/summer months (Fig. 2d) (Belt et al., 2008; Fahl and Stein, 2012). What is more challenging to rationalise according to this model, and given current knowledge, is the occurrence of IP_{25} in sediments from some regions of the central Arctic Ocean (CAO) that experience near-permanent ice cover with little/no ice melt (Xiao et al., 2015a), or some sub-arctic locations such as southeast Greenland and north Iceland, or the South-West Labrador Sea, where sea ice conditions reflect drift ice export from the Arctic Ocean (Massé et al., 2008; Alonso-García et al., 2013; Sicre et al., 2013; Cabedo-Sanz et

al., 2016a; Darby et al., 2017) and (mainly) Baffin/Hudson Bay regions, respectively (Weckström et al., 2013). Further work is therefore still needed to establish a more comprehensive understanding of the conditions under which IP_{25} is produced and the mechanism(s) by which it is exported to underlying sediments.

The source-selective production of IP_{25} by certain sympagic diatoms is further evident from its somewhat enriched stable carbon isotopic composition ($\delta^{13}C$ = ca. -16 to -23‰; summarised in Belt and Müller, 2013) and its general absence in marine surface sediments from regions that experience little or no sea ice cover in modern times (Fig. 2a; Note that the locations of reported IP_{25} absence only indicate those studies where it was specifically analysed for, so likely under-reflects the broader picture of absence). A few exceptions exist, however. For example, IP_{25} has been reported in a small number of surface sediments from locations slightly beyond the modern maximum winter sea ice margin (Navarro-Rodriguez et al., 2013). This may reflect a deviation from strict vertical transport within the water column or re-suspension/advection subsequent to initial deposition in surface sediments (Navarro-Rodriguez et al., 2013). Alternatively, such anomalies may simply reflect the limited resolution of satellite-based determinations of winter (i.e. maximum) ice margins or the uncertainty of the temporal frameworks that surface sediments represent. Further, IP_{25} absence has been noted from some sea ice covered locations, although these are mainly in the CAO where near-perennial sea ice cover prevails (Fig. 2a; Xiao et al., 2015a) and where surface sediments may not adequately reflect recent accumulation. The significance of IP_{25} absence, more generally, is discussed in more detail in the next section.

2.2 Absent IP_{25} – a more challenging scenario to interpret

While a reasonably clear (but not complete) picture for the interpretation of IP_{25} presence is available (Section 2.1), it is less so for IP_{25} absence. In a number of studies, two end-member scenarios for absent IP_{25} have been described, especially in downcore records. The first of these is the occurrence of ice-free conditions, and is reasonable to accept if the source-selectivity of IP_{25} is as believed (i.e. biosynthesis by certain sympagic diatoms only) and is supported by the general absence of IP_{25} in surface sediments from regions of year-round ice-free conditions (*vide supra*; Fig. 2a). The second scenario, of permanent or perennial sea ice cover, requires more assumptions about the conditions by which IP_{25} is (or is not) produced, together with the processes by which it is transferred from sea ice to the sediments. For example, in the seminal work on IP_{25} (Belt et al., 2007), absent IP_{25} in sediments from the northern regions of the Canadian Arctic experiencing near year-round sea ice cover was interpreted as reflecting conditions unsuitable for ice algal growth, release and deposition. However, although accepted at the time, and re-iterated in many subsequent palaeo sea ice reconstructions and in the earlier review by Belt and Müller (2013), this interpretation was, and continues to be, based on supposition only. No targeted investigations aimed at clarifying the production/deposition of IP_{25} under perennial sea ice cover have been carried out, with the exception of the analysis of a suite of sediments from the CAO, which yielded mixed (presence/absence) outcomes (Xiao et al., 2015a; Fig. 2a). As described in the previous section, more work is needed to identify the IP_{25} production and deposition conditions before both presence and absence can be interpreted with complete confidence.

One frequently adopted approach for distinguishing between the permanent versus ice-free end-member scenarios, especially in downcore records, is the co-

measurement of certain other biomarkers, most commonly associated with pelagic phytoplankton. First proposed by Müller et al. (2009), the co-measurement of certain algal sterols, in particular, potentially provides a means of distinguishing between perennial sea ice cover from open water conditions on the basis of relatively low or high phytoplankton biomarker concentrations, respectively. This, of course, makes various assumptions on factors controlling open water productivity and pelagic-benthic coupling, and is further complicated by the biosynthesis of many potential open-water biomarkers from non-pelagic sources. Thus, many sterols can be derived from marine, terrestrial and also sea ice algal sources (Huang and Meinschein, 1976; Volkman, 1986; Volkman et al., 1998; Belt et al., 2013,2018). Further discussion of the role of open-water biomarkers for palaeo sea ice reconstruction can be found in Sections 2.3 and 4.

More generally, IP_{25} absence may reflect a range of sea ice conditions where the (IP_{25}-producing) diatoms are too low in abundance or even absent. Brown et al. (2014c) described the common occurrence of IP_{25}-producers in previously reported taxonomic inventories of sea ice diatoms (Fig. 2c), but there are likely certain scenarios where this is not the case. For example, the lower salinities associated with fjords or near-coastal settings influenced by large river discharges that are common along the Arctic shelves may limit or preclude the colonisation of IP_{25}-producing diatoms in sea ice within such settings, a point made recently by Ribeiro et al. (2017) when interpreting IP_{25} distributions in surface sediments from a NE Greenland fjord, and by others following analysis of IP_{25} in sediments from the Kara and Laptev Seas (Xiao et al., 2013; Hörner et al., 2016). One could also speculate that sea ice with too low of a brine channel percentage or very low surface-to-bottom light transmittance such as thick multi-year ice or ice with substantial snow cover,

could also sufficiently inhibit sympagic diatom growth to an extent that IP_{25} production fails to reach detection levels, as proposed previously (Belt and Müller, 2013); however, such hypotheses remain in need of further research.

Finally, IP_{25} (sedimentary) absence may result from its degradation in sea ice, the water column, in sediments, or a combination of these, as described previously (Belt and Müller, 2013). Alternatively, since ice algal organic carbon (OC) represents an important foodstock at the base of the polar food web, removal of IP_{25} through grazing and subsequent upward trophic transfer may also constrain sedimentary accumulation. Indeed, analysis of IP_{25} (and other HBIs) in primary grazers and higher trophic level consumers has been used with some success to trace the fate of ice algal OC into Arctic and Antarctic marine ecosystems (Brown et al., 2014a,2017a,b,2018; Goutte et al., 2014,2015; Schmidt et al., 2018). Interestingly, amongst these studies, it was shown recently that the relative amounts of IP_{25} and other HBIs remained unaltered between food source, ingested material and faecal pellets when mixed diatom sources were fed to certain *Artemia* sp. (brine shrimp) in laboratory experiments (Brown and Belt, 2017). These preliminary findings suggest that source HBI distributions remain largely unaltered following grazing, which may have positive implications for the use of sedimentary HBI distributional data for palaeo sea ice reconstruction (see Section 4). However, substantially more work is needed before the impacts of grazing on the absolute and relative amounts of IP_{25} and other HBIs in sediments can be fully understood.

In terms of degradative processes, relatively little attention has still been given to this topic, although some laboratory studies have shown IP_{25} to be relatively stable, at least with respect to some other lipids (Rontani et al., 2011,2014b). On the other hand, the susceptibility of IP_{25} towards certain biotic and abiotic degradation

processes was demonstrated recently, following characterisation and detection of various IP_{25} oxidation products in some near surface sediments from the CAA (Rontani et al., 2018a,b). Interestingly, the same degradation processes did not appear to be operating on IP_{25} in the sea ice itself. In contrast, more unsaturated HBIs have been shown to undergo oxidation in Arctic sea ice (Rontani et al., 2014a). However, according to Rontani et al. (2018a), determining the importance of degradation, more routinely, is likely to remain challenging due to the probable secondary reactions of the initial degradation products, which limits their accumulation in sediments.

In summary, I suggest that interpretations of absent IP_{25}, in particular, should be more circumspect, and certainly not limited to the extreme cases of ice-free versus perennial ice cover, which are themselves not sufficiently evidenced, at this point. An overview of how certain sea ice settings are currently believed to influence IP_{25} production is shown in Figure 4.

Finally, although IP_{25} has received the most attention as an HBI sea ice proxy, it is worth noting that its di-unsaturated structural homolog – HBI II (Fig. 1) – is also produced by certain Arctic sympagic diatoms (Brown et al., 2014c). Indeed, IP_{25} and HBI II concentrations are frequently well correlated in Arctic sedimentary records, with the latter normally present in higher concentration. As a result, HBI II has been used as a surrogate for IP_{25} when concentrations of the latter have been close to (or below) the limit of quantification (Andrews et al., 2018). In some reports, variations in the concentration ratio HBI II/IP_{25} or DIP_{25} index have been attributed to either possible changes in temperature or sea ice dynamics (e.g. Vare et al., 2009; Fahl and Stein, 2012; Cabedo-Sanz et al., 2013; Müller and Stein, 2014; Hörner et al., 2016; Ruan et al., 2017); however, the former seems unlikely given the near-uniform

temperatures found at the base of seasonal sea ice where IP_{25} and HBI II are biosynthesised, and no in situ testing of the latter hypothesis has been reported. More fundamentally, apart from the study of Xiao et al. (2013), the relationship between HBI II and sea ice conditions in the Arctic has not been investigated, which is perhaps surprising, given its co-production with IP_{25}. It is thus plausible that HBI II might, in fact, represent a ‘better’ sea ice proxy than IP_{25}, or at least an appropriate substitute in cases where IP_{25} is absent (or below its detection limit). After all, HBI II is proposed as a proxy for Antarctic sea ice (where it is referred to as $IPSO_{25}$), as described in the following section (Section 2.3).

2.3 $IPSO_{25}$ – a proxy measure of Antarctic sea ice

As stated earlier (Section 1.2), IP_{25} has not been identified in Antarctic sea ice or sediments, probably due to the absence of the necessary diatom species. Indeed, none of the IP_{25}-producing species endemic to the Arctic (Section 2.1) have been reported in the Antarctic. However, a di-unsaturated HBI (II; Fig. 1), which co-occurs with IP_{25} in the Arctic (Section 2.2), was first reported in Antarctic sea ice and sediments more than 25 years ago (Nichols et al.,1988,1989,1993), although a definitive source remained elusive at that time and its structure also remained uncertain. Following definitive structural characterisation of this HBI by Johns et al. (1999), Massé et al. (2011) subsequently proposed the use of HBI II as a proxy for Antarctic sea ice and a number of palaeo Antarctic sea ice reconstructions have since followed (Fig. 5b; Table 2). In a more recent study, Belt et al. (2016) identified a source of HBI II as *Berkeleya adeliensis* (Medlin), a common constituent of Antarctic sympagic diatom communities (Medlin, 1990). Consistent with this source, HBI II was also identified in a large number of sediments from near-coastal locations

around the Antarctic continent (Fig. 5a). Given its source identification and widespread sedimentary occurrence, the term $IPSO_{25}$ – ‘Ice Proxy for the Southern Ocean with 25 carbon atoms’ was given to HBI II, by analogy with IP_{25} for the Arctic. It is worth noting, however, that the source-specificity of $IPSO_{25}$ is not as clear-cut as that for IP_{25} since this HBI has also been identified in the benthic diatom *Haslea ostrearia* (Johns et al., 1999; Rowland et al., 2001) and in sediments from some temperate locations (Xu et al., 2006; He et al., 2016). However, a particularly notable characteristic of HBI II in the Antarctic is its distinctive stable carbon isotopic composition, with $\delta^{13}C$ values ranging from ca. -5.7 to -8.5‰ in sea ice samples (Massé et al., 2011). Importantly, ^{13}C-enrichment has also been observed for this HBI in sediments (Sinninghe Damsté et al., 2007, Massé et al., 2011; Belt et al., 2016) and in some near-surface waters proximal to melting sea ice (Schmidt et al., 2018), suggesting a sea ice origin in all cases. Thus, within the context of relatively modern sea ice-covered near-coastal environments around Antarctica, the use of the term $IPSO_{25}$ appears appropriate, for now, at least. However, whether this is also true for offshore locations spanning the entire Southern Ocean, or for older sedimentary sequences where palaeoceanographic conditions may have differed substantially from those of the modern era, remains to be verified. As such, further isotopic measurements of this proxy should probably be carried out as routine, where possible, in order to confirm its origin.

More generally, the development of $IPSO_{25}$ as a proxy for Antarctic sea ice has not received as much attention as that for IP_{25} in the Arctic. Thus, apart from its recent source identification, establishment of its characteristic stable carbon isotopic composition, and its general presence in near-coastal surface sediments, the surface sedimentary distribution of $IPSO_{25}$ has not been calibrated against recent sea ice

conditions (e.g. seasonal sea ice concentrations) in the same way that IP_{25} has been investigated in the Arctic (Section 2.1), and a broader spatial assessment of its distribution has also not been conducted. In fact, as stated earlier, even the distribution of this biomarker in the Arctic has not been investigated in any detail, something that might prove valuable in its development as an Antarctic sea ice proxy.

Exceptionally, Massé et al. (2011) observed a general decline in sedimentary $IPSO_{25}$ concentration in a short offshore transect from East Antarctica; a trend shown subsequently to be quite general for various other Antarctic regions (Belt et al., 2016). In the latter study, it was suggested that the origin of this trend might be found in the preferred habitat of the known source of $IPSO_{25}$ (*B. adelienis*), which has a tendency to proliferate in platelet ice, found most commonly in near-shore locations covered by fast ice (Medlin, 1990). As such, it was hypothesised that higher concentrations of $IPSO_{25}$ might be found in locations proximal to ice-shelves, since their basal melt acts as the major driver for platelet ice formation (Jefferies et al., 1993). Re-examination of some palaeo sea ice records based on $IPSO_{25}$ added further credibility to this suggestion (Fig. 6), and Smik et al. (2016a) also identified highest concentrations of $IPSO_{25}$ in near-shore surface waters soon after spring sea ice melt. Nonetheless, there are still several aspects of proxy development that are in need of attention before the sedimentary signature of $IPSO_{25}$ can be interpreted with greater confidence. These potentially include (but are not limited to): (i) measurement of $IPSO_{25}$ in a larger range of Antarctic surface sediments and comparison of findings with known sea ice conditions; (ii) combining $IPSO_{25}$ concentrations with those of other biomarkers (i.e. similar to the PIP_{25} index used in the Arctic; see Section 4.2); (iii) determination of additional sources (if any) of $IPSO_{25}$

whose habitat(s) may also influence the interpretation of the sedimentary signal; (iv) determination of any diagenetic factors that may impact on the sedimentary profile. For the latter, it is noted that $IPSO_{25}$ was shown to undergo relatively rapid (a few hundred years) incorporation of sulphur in Ellis Fjord (East Antarctica) sediments (Sinninghe Damsté et al., 2007), yet has been readily identified in Holocene and last glacial sediments from other Antarctic regions (Table 2).

Regarding absent sedimentary $IPSO_{25}$, there are likely several potential explanations for this scenario, as described in more detail for absent IP_{25} (see Section 2.2).

2.4 Open water conditions and the marginal ice zone (MIZ)

The third setting for which source-specific biomarkers can potentially provide useful proxy-based information pertinent to seasonal sea ice cover is the region defined by the retreating ice edge or marginal ice zone (MIZ). A number of nuanced definitions of the MIZ exist, and the challenge at arriving at a single description stems from its inherent dynamic behaviour, both spatially and temporally. For the purposes of understanding how biomarker distributions might reflect the MIZ, I consider the definition of Wadhams (1986) to be as good as any. Thus, the MIZ is defined as “that part of the ice cover, which is close enough to the open ocean boundary to be affected by its presence”. For some regions, this approximates to the area bound by the positions of maximum winter and summer sea ice extent, although these are often variable on annual timeframes. For other locations, sea ice dynamics can be far less pronounced or consistent, even on seasonal timeframes, with rapid fluctuations in extent from winter through to summer. These contrasting

scenarios provide important background context for interpretation of biomarker signatures of the MIZ in palaeo records (Section 4).

With such dynamic behaviour, combined with surface ocean settings often characterised by a melange of different sea ice types and open water conditions, the identification of any source-specific biomarkers that represent the MIZ uniquely is an ambitious research objective, to say the least. However, it may be feasible to identify some potential candidates that at least partly align with the key attributes of source-selectivity. For example, a potentially useful starting set of criteria for identification of MIZ biomarkers would be: (i) those that are not found in sea ice; (ii) those that are produced by certain pelagic phytoplankton but do not have additional (e.g. terrestrial) sources; (iii) those whose production is distinct from that found in permanently open waters. The latter could potentially stem from an ecological preference for the nutrient-rich MIZ surface waters or the lower salinities characteristic of the fresh meltwater layer compared to the neighbouring open ocean, although, in practice, this criterion likely represents the most challenging to be satisfied. In addition, the difficulty in identifying any such biomarker(s) is compounded further by the challenges of carrying out representative in situ sampling of the MIZ, not least because of its highly dynamic and often heterogeneous nature. On the other hand, identification of suitable MIZ biomarkers can potentially be deduced from the analysis of surface sediments, even if their accumulation characteristics generally imply an integration of a number of different overlying surface or near-surface conditions spanning several seasons, years, or longer.

In practice, many common algal biomarkers including fatty acids and phytosterols do not satisfy the first two criteria. Indeed, in two recent studies – the first based on fatty acid and sterol distributions in surface waters from East

441 Antarctica, the second based on variable sterol concentration in surface sediments
442 from the Barents Sea and Norwegian Sea in the Eurasian Arctic/subarctic – no
443 significant differences in biomarker abundances or distributions were identified
444 between the respective MIZ and neighbouring open ocean locations (Navarro-
445 Rodriguez et al., 2013; Belt et al., 2015; Smik et al., 2016a). On the other hand, in a
446 number of recent empirical studies, the elevated abundance of a tri-unsaturated HBI
447 biomarker (often referred to as HBI III; Fig.1) in some near-surface waters and
448 surface sediments from the MIZ of certain Arctic and Antarctic regions, suggests that
449 this biomarker may at least part-satisfy several key criteria (Belt et al., 2015; Smik et
450 al., 2016a; Schmidt et al., 2018) (see Fig. 7,8,9 and Tables 1,2 for summaries).
451 Initially, Collins et al. (2013) suggested that sedimentary HBI III might better
452 reflect phytoplankton production in the MIZ compared to the permanently open
453 ocean, based largely on its similar temporal profile to that of the sea ice proxy HBI II
454 (now $IPSO_{25}$) in late glacial sediments from the Scotia Sea (Southern Ocean). In
455 support of this, relatively high concentrations of HBI III have been observed in the
456 near-surface waters of the MIZ in the Scotia Sea (Schmidt et al., 2018) and also off
457 the Sabrina Coast (East Antarctica) (Fig. 8; Smik et al., 2016a). In the Arctic, HBI III
458 concentration was shown to be significantly higher in Barents Sea surface sediments
459 from locations normally associated with the MIZ, at least compared to those settings
460 that experience ice-free or mainly year-round ice cover (Fig. 9; Belt et al., 2015). In
461 addition, in a study of biomarker content in a small number of surface sediments
462 from a NE Greenland fjord, HBI III was most abundant for locations proximal to the
463 mid-July ice edge (Ribeiro et al., 2017).
464 Several *Rhizosolenia* spp. isolated from polar and sub-polar locations from
465 both hemispheres (Belt et al., 2017) have recently been identified as sources of HBI

III, whose isotopic composition, when detected in polar environments ($\delta^{13}C$ = ca. -35 to -40‰; Massé et al., 2011; Smik et al., 2016a; Schmidt et al., 2018), is also consistent with production by pelagic, rather than sympagic, algae. Combined, these background studies, albeit relatively small in number thus far, indicate that HBI III may prove to be a useful proxy measure for the MIZ in the Arctic and the Antarctic, for some locations, at least. In terms of selection criteria, although the biosynthesis of HBI III by certain pelagic diatoms is clear, the reason for its enhanced production within the MIZ is not evident at this stage and is in need of further attention. Potentially, increased production might reflect an environment-specific response. For example, the nutrient-rich conditions normally associated with the MIZ may particularly favour the growth of *Rhizosolenia* spp., or at least the biosynthesis of HBI III by such species. The possibility of HBI III biosynthesis by other polar pelagic diatoms should also be considered, although only certain *Pleurosigma* spp. have previously been shown to be producers of this HBI, and such species are not especially common or abundant in polar environments. For now, therefore, the use of HBI III as a MIZ proxy is based largely on the aforementioned empirical observations. As for absent HBI III, while it is tempting at this stage to interpret this scenario in terms of permanent sea ice cover due to little or no pelagic algal production, it may also result from an absence (or too low abundance) of the HBI III-producing diatoms in some settings/time intervals, or degradation in the water column or sediments. The co-measurement of other phytoplanktic biomarkers is, therefore, probably still useful in terms of elucidating productivity trends, more generally. In the meantime, some suggestions for how the production of HBI III might be dictated by different Arctic sea ice settings is shown in Figure 4.

3. Analytical considerations

Central to the use of source-specific HBIs as sea ice proxies is the reliability of the analytical measurement, which includes both accurate identification and quantification. The former should be straightforward given the availability of suitable laboratory standards, well-maintained GC–MS instrumentation and published chromatographic and mass spectral data, but care should still be taken, not least given the similar chromatographic and mass spectral properties of many HBIs. For example, Cabedo-Sanz and Belt (2015) identified a C_{25} HBI monoene in ancient Arctic sediments, which has a very similar GC retention index and mass spectrum to that of IP_{25}, but has not thus far been reported in sea ice. Further, for Arctic sediments, which commonly contain both IP_{25} and its di-unsaturated pseudo-homolog HBI II (Fig. 1), the near isobaric nature of their molecular ($M^{+\cdot}$) and $(M+2)^{+\cdot}$ ions, respectively (both nominally *m/z* 350) (Fig. 10), together with their very similar retention indices on non-polar stationary GC phases (e.g. RI_{HP5ms} 2081 and 2082 for IP_{25} and HBI II, respectively; Belt and Cabedo-Sanz, 2015), provides an opportunity for mis-identification, especially of IP_{25}. In fact, during an inter-laboratory investigation of IP_{25} and other HBIs (Belt et al., 2014), IP_{25} was sometimes incorrectly identified in an Antarctic sediment (i.e. one known not to contain IP_{25}), where HBI II was present in sufficient abundance for its $(M+2)^{+\cdot}$ ion to be readily detected and mis-assigned to the $M^{+\cdot}$ ion of IP_{25}. Such mis-identification could arguably be attributed to the blind nature of the sediments under study (the participants were not aware of the origin of the sediments), but this cautionary tale is nonetheless useful for future analyses.

Ambiguity in HBI identification may potentially become more problematic for more unsaturated HBIs, due to the larger number of isomeric forms biosynthesised

by diatoms (Belt et al., 1996,2000,2001; Grossi et al., 2004; Poulin et al., 2004; Brown and Belt, 2016), the extremely similar mass spectra generally seen for isomeric HBIs (Belt et al., 2000; Brown and Belt, 2016), and the difficulties in often obtaining high quality total ion current mass spectra from analysis of sediment extracts, in any case, due to low abundances or spectrometric interferences. Accurate identification is especially important, however, since only one of the structurally characterised HBI trienes (HBI III; Fig. 1) has been firmly associated with the MIZ in the Arctic and Antarctic. A brief perusal of some reports of HBI III suggests that it may have been mis-identified based on the literature cited when describing it’s characterisation.

The inter-laboratory study of sedimentary IP_{25} (Belt et al., 2014) revealed further analytical considerations important to its accurate identification and quantification (and of other HBIs). For example, significant differences in instrumental (GC–MS) response factors were observed between individual laboratories (by up to a factor of 2–6), with further differences noted for the two internal standards employed (7-hexylnonadecane (7-HND) and 9-octylheptadec-8-ene (9-OHD)) and the specific biomarker ions selected for quantification. In the Plymouth laboratory, both of these IS are used for HBI quantification purposes, with routine monitoring of biomarker-specific GC–MS response factors performed through analysis of (i) a homogenised sediment with known HBI concentration and (ii) a series of standard solutions of variable HBI concentration. The first approach was indeed a recommendation following the inter-laboratory investigation of IP_{25} (Belt et al., 2014), yet it is not always evident how such response factors are measured (if at all) in a number of published studies based on IP_{25} and other HBIs, or how final sedimentary concentrations using these are arrived at. While this may not be critical

when only interpreting relative changes to IP_{25} (and other HBI) concentration in an individual downcore sequence, or when converting individual biomarker data into PIP_{25} indices (Section 4.2), it does have implications when making comparisons between absolute biomarker concentrations obtained from different laboratories. For example, in assessing some pan-Arctic IP_{25} (and PIP_{25}) data compiled from new and various published datasets, Xiao et al. (2015a) elected to omit some previously reported IP_{25} data by Stoynova et al. (2013) on the basis of unusually high values, which might have resulted from the employment of a different analytical method. As such, it is recommended that all aspects of HBI identification and quantification (i.e. GC retention indices, mass spectral data, methods for calculating GC responses factors, etc.) are reported in future studies, wherever possible.

The inter-laboratory study by Belt et al. (2014) also provided a brief assessment of two different extraction methods commonly used in HBI and other biomarker analysis. In brief, while similar results were obtained for IP_{25}, $IPSO_{25}$ and the internal standard 7-HND (Fig. 1) when using accelerated solvent extraction (ASE) or sonication (DCM/MeOH) methods, some degradation of more unsaturated HBIs (e.g. HBI III) and the internal standard 9-OHD (Fig. 1) was observed using the former method, possibly due to the higher temperatures employed. In addition, the effects of storage conditions on the stability of IP_{25} and other HBIs in sediments and sediment extracts has also been briefly investigated (Cabedo-Sanz et al., 2016b) following the recommendation of Belt and Müller (2013). In summary, over a two year study period, tri-unsaturated HBIs such as HBI III were shown to be more susceptible to degradation than IP_{25}, especially when sediments were stored in plastic bags and exposed to light at room temperature. In contrast, all HBIs were relatively stable in sediments stored in glass vials and kept frozen in the dark. It was

566 also demonstrated that analysis of long-term stored sediment extracts could also
567 lead to anomalous results, even when kept at low temperature (-20°C) (Cabedo-
568 Sanz et al., 2016b).

569 A final point pertinent to the analytical measurement concerns the
570 identification of the most appropriate threshold concentration of IP_{25} or $IPSO_{25}$ for
571 sea ice inference, especially if primary interpretations, as described here, are based
572 within a binary framework of sea ice presence/absence. To my knowledge, such a
573 threshold has yet to be identified and reported absences of IP_{25} potentially reflect
574 limits of detection or quantification rather than strict absence. This point was already
575 discussed in some detail by Belt and Müller (2013), but has received little or no
576 further attention since then. In the Plymouth laboratories, we define absence as
577 being below the limit of quantification using current GC–MS instrumentation
578 (equivalent to 0.05 ng/g dry weight sediment) following extraction from a maximum of
579 5 g dry sediment. However, this definition simply ensures in-house consistency
580 between investigations.

581

582 **4. Reading the sedimentary record – converting biomarker profiles to**
583 **qualitative and semi-quantitative sea ice reconstructions**

584

585 Having described the characteristics of various source-specific HBI sea ice
586 and MIZ biomarkers (Section 2), the following sections provide an overview of how
587 the individual and combined biomarker profiles recorded in various palaeo records
588 are routinely interpreted to provide qualitative and semi-quantitative estimates of
589 past sea ice conditions.

590

591 *4.1 Individual biomarker profiles*

592 In general, the starting point for palaeo sea ice reconstructions based on
593 source-specific HBIs (and some other biomarkers) is analysis of their individual
594 concentration variability in well-dated downcore records. In the case of IP_{25}, the
595 principle of higher sedimentary concentrations being indicative of ‘increased sea ice
596 concentration/extent/cover’ as a qualitative outcome is widely applied, and has its
597 foundation in the first downcore IP_{25} record from North Iceland, where Massé et al.
598 (2008) identified excellent agreement between sedimentary IP_{25} concentration and
599 historical (observational) sea ice records. Subsequent reports of surface sedimentary
600 distributions also mainly reflect this relationship (Section 2.1; Table 1), which is
601 sometimes supported further by data from other sea ice proxies (e.g. ice-rafted
602 debris; IRD) or those that reflect complementary oceanographic conditions such as
603 sea surface temperature (SST). However, the relationship between sedimentary IP_{25}
604 concentration and overlying sea ice conditions is not normally linear (or any other
605 simple function) and regional variability in IP_{25} concentration for equivalent sea ice
606 cover is significant (Stoynova et al., 2013; Xiao et al., 2015a). Some of this variability
607 may reflect differences in individual laboratory methodology as described earlier
608 (Section 3) and previously by Xiao et al. (2015a). Further, it has been suggested that
609 primary productivity (in sea ice) might be a more important factor than sea ice extent
610 in terms of determining sedimentary IP_{25} concentration (Belt and Müller, 2013;
611 Cormier et al., 2016).

612 Nonetheless, the now quite extensive set of regional ‘calibrations’ spanning
613 various Arctic and sub-Arctic regions provides some support to the general principle
614 that directional changes in sedimentary IP_{25} concentration likely reflect
615 corresponding changes in sea ice extent, even if only qualitatively (Belt and Müller,

2013). The ambiguities associated with interpreting absent IP_{25} are potentially even more problematic than with surface sediment analysis, which at least have known modern conditions to serve as reference. On the other hand, distinguishing perennial sea ice cover from ice-free settings (the most common interpretations of absent IP_{25}) can potentially be resolved by consideration of other biomarkers indicative of the open water setting (see Sections 2.2, 2.4 and 4.2).

For the Antarctic, palaeo sea ice reconstructions based on $IPSO_{25}$ (often referred to as HBI II in previous publications) have mainly assumed a positive relationship between biomarker concentration and sea ice extent, with complementary proxy data (e.g. SST) provided in some cases (Table 2). However, as described earlier (Section 2.3), no calibration studies comparing $IPSO_{25}$ distributions with known sea ice cover have, as yet, been carried out, so the assumption of increased $IPSO_{25}$ reflecting higher sea ice extent is based almost entirely by analogy with IP_{25} in the Arctic. Further, it has been suggested that the ecology of *B adeliensis* (one of the sources of $IPSO_{25}$) might be the major influence over its sedimentary distribution (Belt et al., 2016). What is evident from the relatively small number of previous investigations, however, is that considerably more work is required before the sedimentary signature of $IPSO_{25}$ can be fully understood, and at least before any unequivocal comparisons with IP_{25} for the Arctic can be made. Determining the distributional pattern of this biomarker in Arctic sea ice and sediments may also prove useful in this respect (Section 2.2).

Interpretations of HBI III profiles in palaeo records are probably most meaningfully carried out alongside their IP_{25} (and $IPSO_{25}$) counterparts, especially given their respective signatures of the MIZ and sea ice. As background, relatively high (low) IP_{25} concentrations were identified in surface sediments from study sites in

641 the Barents Sea experiencing high (low) spring sea ice concentration, while the
642 opposite trend was observed for the abundance distribution of HBI III, consistent with
643 its higher production in the MIZ following rapid ice margin retreat during the spring
644 (Fig. 9; Belt et al., 2015). This contrasting behaviour was also evident in some
645 palaeo IP_{25} and HBI III records from the region, with high IP_{25} concentration
646 coincident with low HBI III over some sedimentary time intervals and vice versa in
647 others (Fig. 11). Such changes were interpreted as reflecting temporal shifts to the
648 positions of the winter/summer ice margins within an otherwise annual cycle of sea
649 ice advance/retreat (Belt et al., 2015; Berben et al., 2017).

650 Although this out-of-phase behaviour of IP_{25} and HBI III in some temporal
651 records is consistent with surface sediment distributions that reflect modern-day
652 regional sea ice dynamics, it is not always evident in some other downcore archives.
653 In fact, positively correlated or ‘in-phase’ IP_{25} and HBI III profiles were reported in
654 some recent reconstructions (Fig. 11), including part of a recent century sea ice
655 record from western Svalbard (Cabedo-Sanz and Belt, 2016), two recent
656 interglacial/glacial records from the Yermak Plateau/Barents Sea continental margin
657 (Stein et al., 2017a; Kremer et al., 2018b), and certain timeslices associated with the
658 Mid-Pleistocene Transition in the Bering Sea (Detlef et al., 2018). In these cases, the
659 switch to in-phase biomarker behaviour was attributed to rapidly fluctuating sea ice
660 conditions or the presence of an offshore polynya; environments that likely had
661 parallel influence over sea ice (IP_{25}) and ice-influenced (HBI III) biomarker production
662 (see Section 2.4). Prior to these relatively recent studies, in-phase temporal changes
663 between IP_{25} and certain phytoplankton sterol concentrations in downcore records
664 was also interpreted in terms of a rapidly advancing and retreating sea ice margin
665 (Müller et al., 2009,2011,2012).

To date, however, this interpretation has not been investigated further via in situ measurements of sea ice and the surface waters of the MIZ, but analysis of surface sediments from western Svalbard – a region known to experience rapid year-round fluctuations in sea ice conditions in modern times – revealed a similar positive relationship between IP_{25} and HBI III (Smik and Belt, 2017). Otherwise, apart from the analysis of IP_{25} and HBI III in a relatively small number of surface sediments from two Greenland fjords (Ribeiro et al. 2017; Limoges et al., 2018), there have been no additional investigations into their distributions in surface sediments from other Arctic regions, and none in any detail. As such, it is not clear how representative the two contrasting observations and interpretations of Barents Sea (and neighbouring regions) biomarker distributions are for other northern high-latitude locations. In the meantime, some further palaeo IP_{25} and HBI III records from North Iceland and the Sea of Okhotsk have been reported, although their temporal phase relationships were not interpreted in any detail (Cabedo-Sanz et al., 2016a; Xiao et al., 2017; Lo et al., 2018).

In the Antarctic, Collins et al. (2013) discussed the contrasting temporal phase relationships between $IPSO_{25}$ and HBI III in glacial sediments from the Scotia Sea, adding an element of seasonality to the interpretations. Thus, intervals where $IPSO_{25}$ and HBI III were most positively correlated (i.e. strongly in-phase) were interpreted in terms of semi-permanent or stationary sea-ice margins with low seasonality and coupled impact on the respective sea ice and MIZ biomarkers. Conversely, during times of high sea ice seasonality, production of $IPSO_{25}$ and HBI III became more decoupled. To some extent, these changes replicate the variable (relative) behaviour of IP_{25} and HBI III in surface and downcore sedimentary records from the Barents Sea, as described above. However, other downcore profiles of $IPSO_{25}$ and HBI III

691 from the Antarctic have been interpreted largely in terms of increases/decreases to
692 sea ice extent with concomitant reverse trends in open water conditions (Table 2).
693 Re-examination of some of those records might provide further insights into palaeo
694 sea ice dynamics now that the relationship(s) between sea ice (IP_{25} and $IPSO_{25}$) and
695 HBI III are better understood.

696 Finally, an unresolved question, and one raised initially by Belt and Müller
697 (2013) in an earlier review, concerns the most appropriate units for expressing IP_{25}
698 (and other HBI) sedimentary content in downcore records. The three most frequently
699 used are (i) mass (HBI)/mass dry sediment; (ii) mass (HBI)/total organic carbon
700 (TOC); (iii) flux (HBI). Each approach has been used in previous HBI-based
701 investigations, although a clear justification for their selection is not always evident.
702 Since each has different merits (Belt and Müller, 2013), obtaining similar outcomes
703 from each approach likely goes part way to resolving which is the most appropriate
704 for a given study. On the other hand, combining individual biomarker concentrations
705 using relatively simple ratio-based approaches, or more detailed distribution-based
706 methods, simplifies the debate considerably. This is addressed, in further detail, in
707 the next section.

708

709 *4.2 Combining biomarkers – from the PIP_{25} index to multivariate analysis*

710 The second step normally taken when interpreting sea ice (and related)
711 biomarker data is application of one or more combinative approach. Relatively
712 simple biomarker ratio-based methods are common, of course, in organic
713 geochemistry, most notably within palaeo-oceanographic investigations of surface
714 and sub-surface SSTs via the U^{K}_{37} and TEX_{86} indices (Brassell et al., 1986; for
715 reviews, see Eglinton and Eglinton, 2008; Schouten et al., 2013). For biomarker-

based palaeo sea ice studies, such combinative approaches have thus far only been employed for the Arctic and, until recently, have focussed entirely on the so-called PIP_{25} index. First introduced by Müller et al. (2011), the PIP_{25} index combines the relative concentrations of IP_{25} and a selected phytoplankton biomarker (designated P) according to Eqn. 1 (square brackets denote concentrations). The *c* factor is the ratio of the mean concentrations of IP_{25} and P for all sediments under study (i.e. Eqn. 2) and was introduced by Müller et al. (2011) to accommodate the normally much higher concentrations of phytoplanktic lipids (P) compared to IP_{25}.

$$PIP_{25} = \frac{[IP_{25}]}{([IP_{25}] + c[P])} \#(1)$$

$$c = \frac{mean[IP_{25}]}{mean[P]} \#(2)$$

$$P_{III}IP_{25} = \frac{[IP_{25}]}{([IP_{25}] + 0.63[III])} \#(3)$$

$$SpSIC\ (\%) = \frac{(P_{III}IP_{25} - 0.0692)}{0.0107} \#(4)$$

As a result, all PIP_{25} indices fall within the range 0–1, which potentially addresses some of the difficulty in interpreting larger-scale variability in absolute biomarker concentrations as described earlier (Section 4.1). In general, higher PIP_{25} values are interpreted in terms of higher sea ice concentration or extent, on the assumption that primary production is biased towards IP_{25} under such conditions. At the upper limit,

734 PIP_{25} = 1 implies biosynthesis of IP_{25} but no phytoplankton (or selected biomarker)
735 production, which is rarely, if ever, the case. Conversely, the lower limit (i.e. PIP_{25} =
736 0) is arrived at for absent (or below the detection limit) IP_{25}, which has been
737 frequently been interpreted as representing either ice-free conditions or permanent
738 ice cover. However, the latter interpretation, at least, likely needs re-consideration
739 given the occurrence of IP_{25} in some sediments from regions of permanent sea ice
740 cover (Xiao et al., 2015a) and for other reasons outlined earlier (Section 2.2). It
741 should also be noted that, if the assumption of absent IP_{25} for ice-free or perennial
742 ice cover is correct, then the PIP_{25} index cannot be used to distinguish between
743 these two end-members, since PIP_{25} is equal to zero in each case. However, on
744 some occasions where IP_{25} and phytoplankton markers have been found to be
745 extremely low/absent (presumed to reflect heavy/perennial sea ice conditions), PIP_{25}
746 has sometimes been set to 1, which is potentially mis-leading. Under such
747 circumstances, interpretations based on the individual biomarkers are probably more
748 robust.

749 The reliability of the PIP_{25} index as a semi-quantitative measure of Arctic sea
750 ice conditions remains a topic of debate for all of the reasons described by Belt and
751 Müller (2013) and a further detailed account is not warranted here. In brief, the
752 accuracy of the PIP_{25} index for semi-quantitative sea ice prediction depends on (i)
753 the region of study; (ii) the choice of phytoplanktic marker (and whether it has a strict
754 pelagic origin); (iii) the algorithmic relationship between PIP_{25} and sea ice conditions
755 (e.g. linear, logarithmic, etc.); (iv) the *c* factor; (v) the temporal interval in downcore
756 records (which impacts on the *c* factor).

757 Despite the general lack of progress in the development of the PIP_{25} index
758 since it was first reviewed by Belt and Müller (2013), some positive features can

nonetheless be identified. For example, although in the majority of studies PIP_{25} profiles simply resemble the corresponding IP_{25} trends (or at least do not reverse them), the conversion of univariate IP_{25} and P concentration data to a uniform scale is probably useful for consistency and comparison purposes. The ratio-based method also removes any need to identify the most appropriate units for the individual biomarker concentrations or fluxes, since any denominator used in such terms is eliminated, algebraically, a point unfortunately missed in a recent assessment of the impacts of different units on PIP_{25} indices (Pieńkowski et al., 2017). Further, for one particular region (the Barents Sea), the use of HBI III as the phytoplanktic counterpart to IP_{25} when calculating PIP_{25} indices (hereafter $P_{III}IP_{25}$) has been shown to alleviate, to a large extent, most of the frequent drawbacks associated with points (i)–(v) above. In particular, the more closely matched sedimentary IP_{25} and HBI III concentrations, at least in sediments from the Barents Sea, somewhat limits the variability in the *c* factor, and a fixed value for *c* was proposed based on a regional calibration (Smik et al., 2016b). The benefit of a fixed *c* factor, in particular, ensures that $P_{III}IP_{25}$ indices at individual sedimentary timepoints remain fixed, and are independent of the overall time interval under study, something that is not the case when *c* is calculated on a piecemeal basis, as discussed previously (Belt and Müller, 2013). Xiao et al. (2015a) also proposed the possible use of a pan-Arctic c factor derived from analysis of surface sediments from different Arctic/sub-arctic regions; however, this value is not especially representative for any particular region and has not been used in more recent palaeo sea ice reconstructions.

In addition, the only known sources of HBI III are marine diatoms, thus making it a more selective phytoplanktic contributor to PIP_{25} index calculations, while its

apparently higher production within the MIZ (Section 2.4) also aligns well with the underlying principles of the PIP_{25} index, with a switch-over in biomarker responses between the two end members of sea ice cover and open water settings (Fig. 4). In fact, the switch from higher IP_{25} (sea ice) to increased HBI III (MIZ) is exemplified further from the good linear relationship between $P_{III}IP_{25}$ and spring sea ice concentration (SpSIC) (Eqn. 4) for the Barents Sea (Smik et al., 2016b). A minimum threshold for summer sea ice occurrence ($P_{III}IP_{25} > 0.8$) was also proposed (Smik et al. 2016b). Semi-quantitative estimates of SpSIC (and changes thereof) in early to late Holocene records from the region have subsequently been reported (Cabedo-Sanz and Belt, 2016; Berben et al., 2017). However, although some further records of HBI III have been reported from other Arctic and subarctic regions (Stein et al., 2017a; Kremer et al., 2018b; Lo et al., 2018), none have so far been used to calculate $P_{III}IP_{25}$ indices using a fixed *c* factor derived from a regional calibration, or for more quantitative SpSIC estimates. Before this is carried out, it is recommended that further regional scale calibrations are conducted in order to establish the generality (or otherwise) of the approach.

Despite the success of using HBI III as a phytoplankton biomarker for the PIP_{25} index, as described above, uncertainties regarding selection of the most appropriate phytoplanktic biomarker, more generally, remain. Further, it is still not clear whether the PIP_{25} method is even applicable in some regions, and the problems associated with biomarker co-variance, as discussed previously (Müller et al., 2011,2012; Belt and Müller, 2013), also persist. Under such circumstances, PIP_{25} indices remain largely invariant, despite potentially significant changes to sea ice conditions.

To take a different approach, Köseoğlu et al. (2018b) recently investigated the potential of multivariate non-parametric methods for calibrating biomarker distributions against sea ice conditions. Such approaches make no *a priori* assumptions about the ‘best’ biomarker for individual settings (sea ice, MIZ, open water, etc), although some pre-selection of potential candidates is judicious. In the current context, only HBIs with known sympagic and pelagic sources were selected, with exclusion of other lipid classes potentially derived from other (e.g. terrestrial) environments. In the classification tree (CT) approach adopted by Köseoğlu et al. (2018), a suite of HBI distributional data obtained from surface sediment analysis (the so-called descriptive or independent variable) was first used to create a model from which the target (or dependant) variable could be predicted; in this case, semi-quantitative categorical descriptions of sea ice extent (Fig. 12a). The output from this calibration consists of a relatively simple threshold criteria tree structure (Fig. 12b) from which any new distribution of biomarkers can be readily interpreted. In fact, a further feature of the CT model approach is the visually intuitive nature of the data output. Using surface sediment biomarker data from ca. 200 locations across the Barents Sea and neighbouring regions, Köseoğlu et al. (2018b) showed that the variable distributions of relatively simple assemblages of HBI lipids (typically 4–6 HBIs) could provide consistent predictions of three different classes of sea ice conditions, with high accuracy. Indeed, model performance data are standard outputs from CT methods. Perhaps not surprisingly, given previous investigations, IP_{25} was found to be a primary predictor of sea ice cover in the Barents Sea, with HBI II (co-produced with IP_{25} in the Arctic) as a surrogate variable in cases where IP_{25} might be absent (or below the detection limit). Interestingly, for the MIZ or open water settings, the geometric isomer of HBI III (i.e. IV; Fig. 1) was identified as the

main predicting variable (with HBI III as a surrogate), even though it was normally present in higher concentration. Further, based on analysis of a suite of HBIs in some relatively short cores spanning recent centuries from different regions of the Barents Sea (Fig. 12c), CT model predictions of sea ice conditions showed good agreement with those recorded in historical records, and also with $P_{III}IP_{25}$-based estimates of SpSIC (Fig. 12d).

Some potential disadvantages of the CT approach are discussed in more detail by Köseoğlu et al. (2018a,b) so only a few are described in brief here. First, as with the PIP_{25} index, it is almost certainly a requirement that individual CT models are created (and tested) for different regions, not least, because the precise distributions of biomarker sets may depend on factors other than sea ice, depending on location.

Second, distributional variations observed in surface sediments reflecting modern sea ice conditions may not always be replicated in downcore records, especially if sea ice conditions in the past do not have a parallel for the region in modern times. For example, this might be important in the case of permanent sea ice cover in the Barents Sea (e.g. during glacial intervals), for which there is no contemporary analogue. A further mis-match between modern and palaeo distributions might also result if differential biomarker degradation is significant. Thus, although the relative sedimentary stability of IP_{25} and HBI III has not been investigated, the latter has been shown to be more susceptible to oxidative degradation in laboratory experiments (Rontani et al., 2011, 2014b) and probably also in the water column (Rontani et al., 2016). Of course, differential biomarker degradation will also likely impact on other biomarker-based approaches. Although these factors are in need of detailed investigation in the future, it is interesting to note

that, in a recent study, Köseoğlu et al. (2018a) showed that CT model-based reconstructions of sea ice conditions for three sub-regions of the Barents Sea over the last ca. 16 cal. kyr BP were, in fact, in good agreement with those obtained from other proxy data, suggesting that this multivariate approach does, indeed, have potential within the palaeo record.

Third, the employment of unique threshold values for distinguishing individual sea ice classifications (see Fig. 12b) necessitates the accurate quantification of all biomarkers under study. In this sense, the routine determination of GC–MS response factors (see Section 3) is paramount and it cannot be assumed that these will be equivalent (or even similar) for all HBIs, despite their similar structures (Belt et al., 2014). This is less of a concern when calculating PIP_{25} indices according to Eqn. 1 and 2, since the *c* factor will automatically accommodate any differences. However, accurate biomarker quantification is essential if a fixed *c* factor is used (see Section 4.2). Some specific examples of the impacts of inaccurate biomarker quantification on CT model output can be found in Köseoğlu et al. (2018a).

Finally, using biomarker distributions to predict broader classifications of sea ice extent (e.g. 0–10%,10–50%, 50–100%; Fig. 12) is arguably a more realistic or reliable target than integer-resolution SpSIC estimates from PIP_{25} index calibrations.

5 Knowledge gaps and areas for future research

Since the first review of IP_{25} and other HBIs by Belt and Müller (2013), some clear progress has been made towards their development as sea ice proxies, but some knowledge gaps remain or have since emerged. Thus, specific diatom sources for IP_{25}, $IPSO_{25}$ and HBI III have been identified (Sections 2.1, 2.3, 2.4), some regional calibrations of single and combined biomarker distributions versus sea ice

883 conditions have been completed, and a suite of palaeo sea ice reconstructions
884 based on these biomarkers have been reported spanning different regions and
885 timeframes (Tables 1 and 2). On the other hand, as alluded to at various points
886 within this review, some further work is needed before the full potential of source-
887 specific HBIs can be realised. These likely represent ab initio investigations such as
888 determination of the factors that control production, deposition and preservation of
889 HBIs, while others are more empirical in nature, like the further regional calibration of
890 HBI distributions in surface and downcore records, both of which also make
891 assumptions about the nature of the reference data (e.g. accuracy of satellite-based
892 sea ice extent data, surface sediment timeframes, etc). In writing this review, a
893 number of such future research areas came to mind, but only a few are described in
894 brief here.

895 First, there is the need for a larger spatial assessment of IP_{25} and $IPSO_{25}$
896 production by Arctic and Antarctic sea ice diatoms, respectively. Currently, this has
897 been confined to an extremely small number of locations (Fig. 2c,5c), yet palaeo
898 records based on these HBIs are emerging rapidly from both polar regions. In similar
899 vein, the analysis of IP_{25} and $IPSO_{25}$ in different ice types (e.g. first-year ice, multi-
900 year ice, landfast ice, drift ice, platelet ice, etc) will likely provide further insights into
901 how sedimentary distributions might be better interpreted. Second, further regional
902 calibrations of combined biomarker datasets (e.g. the PIP_{25} index or CT models)
903 against known sea ice conditions would add further confidence in their application for
904 palaeo reconstruction purposes. In this sense, as demonstrated quite recently for
905 HBI III in certain Arctic and Antarctic regions, there may be further (better) pelagic
906 biomarkers that act as suitable counterparts to IP_{25} and $IPSO_{25}$ for characterisation
907 of the MIZ, or open waters in the polar regions, more generally. The measurement of

a range of biomarkers under in situ conditions (e.g. in the water column and in sediment traps) would certainly promote the development of this area and potentially help clarify the significance of their contrasting spatial and temporal phase relationships as described here (Sections 2,4). There may also be further statistical approaches that help decipher the origins of certain biomarkers on a case-by case basis rather than extrapolation of findings from previous studies, which might not be relevant, environmentally. Third, greater efforts should be made to ensure the accurate identification and quantification of all HBIs (and other biomarkers for that matter), which includes the subsequent reporting of these in research outputs – this is also true for output from my own laboratory. Fourth, it would be valuable for more comparison studies of different sea ice proxies to be carried out. Thus far, these have been relatively few (Table 1) and interpretations have largely centred around trying to establish which is the ‘best’ proxy, rather than aiming to understand the potential nuances between them; however, this is not a trivial task.

6. Concluding remarks

The source-selectivity of IP_{25} and $IPSO_{25}$, in particular, represents an important characteristic in terms of their suitability as sea ice proxies. Of course, one might argue that these biomarkers more accurately represent proxy measures of their sympagic diatom sources than of sea ice per se, and some previous descriptions of IP_{25} and $IPSO_{25}$ as ‘direct’ proxies of sea ice are possibly over-stated, especially given the various unresolved caveats governing their production and fate described herein. On the other hand, gaining a better understanding of the environmental conditions that influence IP_{25} and $IPSO_{25}$ production could potentially enhance their value as sea ice proxies, as described in more detail by Belt et al.

(2016). It is also worth noting that biosynthesis of IP_{25} and $IPSO_{25}$ by sympagic diatoms does not unequivocally enhance their usefulness as sea ice proxies, and other ‘less direct’ methods may be more robust in some settings. On the other hand, their source-selectivity appears to provide a reasonably secure positive (seasonal) sea ice signature, even if only qualitatively. In any case, the identification of the boundary conditions for the formation and sedimentary deposition of IP_{25} and $IPSO_{25}$ represent important next-stage objectives. The extent to which qualitative outcomes can be routinely and reliably translated into more quantitative or nuanced descriptions of sea ice conditions also constitutes an interesting but challenging research area.

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Figures

Figure 1. Structures of HBI biomarkers discussed in this review. The structures of two internal standards often used in the quantification of HBIs are also shown.

Figure 2. Summary maps of locations where IP_{25} has been investigated for proxy development and palaeo Arctic sea ice reconstruction purposes: (a) surface sediments; (b) palaeo sea ice studies (c) sea ice, sea ice algae and taxonomic studies where the IP_{25}-producing diatoms have been reported; (d) sediment trap (sinking particulate matter) and water column (suspended particulate matter) samples. See Tables 1,2 for more details.

Figure 3. Temporal changes in IP_{25} concentration in Arctic sea ice from the Amundsen Gulf (2008; red symbols, dotted line) and Resolute Passage (2011: green symbols, solid line; 2012: blue symbols, dashed line) showing peak production in spring (May–June). The outer ordinate scale corresponds to data from the Amundsen Gulf and Resolute Passage (2011); the inner scale refers to data from Resolute Passage (2012). Note the parallel trends between IP_{25} and Chl a, a bulk measure of ice algal primary production. A map showing the approximate sampling locations is also shown. Adapted from Belt et al. (2013).

Figure 4. Schematic representation summarising the proposed relative abundance production of IP_{25} and HBI III in different near-surface oceanographic settings within the Arctic. Note that some scenarios (e.g. a constantly fluctuating sea ice margin) are not shown. In brief, IP_{25} production is known to take place in

seasonal sea ice prior to melting and ice margin retreat in spring (see also Fig. 3; Brown et al., 2011; Belt et al., 2013). According to sedimentary distributions, highest IP_{25} concentration is normally associated with more frequent or long-lasting seasonal sea ice, with moderate/high levels also found for regions proximal to the sea ice edge or the marginal ice zone (MIZ), including polynyas. In contrast, IP_{25} production in multi-year ice, thick snow-covered ice, etc, is likely very low (or absent) but is in need of further investigation. IP_{25} is not believed to be produced in open waters. Production of HBI III is thought to be limited to ice free conditions, with highest concentrations associated with the open waters of the MIZ (Belt et al., 2015). Please refer to Sections 2.1, 2.2 and 2.4 of the main text for more detailed descriptions.

Figure 5. Summary maps of locations where $IPSO_{25}$ has been investigated for proxy development and palaeo Antarctic sea ice reconstruction purposes: (a) surface sediments; (b) palaeo sea ice studies; (c) sea ice and taxonomic reports of *Berkeleya adeliensis* (a source of $IPSO_{25}$); (d) water column (phytoplankton) samples. See Tables 1,2 for more details.

Figure 6. Examples where analysis of $IPSO_{25}$ (HBI II) has been used to reconstruct palaeo Antarctic sea ice conditions for the West Antarctic Peninsula spanning different timeframes. The blue shaded areas correspond to intervals of elevated $IPSO_{25}$ concentration that also coincide with periods of glacial meltwater or ice shelf influence as derived from other proxy records. Figure adapted from Belt et al. (2016); data taken from Barbara et al. (2013,2016) and Etourneau et al., 2013.

Figure 7. Summary maps showing locations where HBI III has been investigated for proxy development and palaeo sea ice (Marginal Ice Zone) purposes: (a) Arctic surface sediments; (b) Arctic palaeo records and water column studies; (c) Antarctic surface sediments; (d) Antarctic palaeo records and water column studies. All studies were carried out on sediment material unless otherwise indicated. See Tables 1,2 for more details.

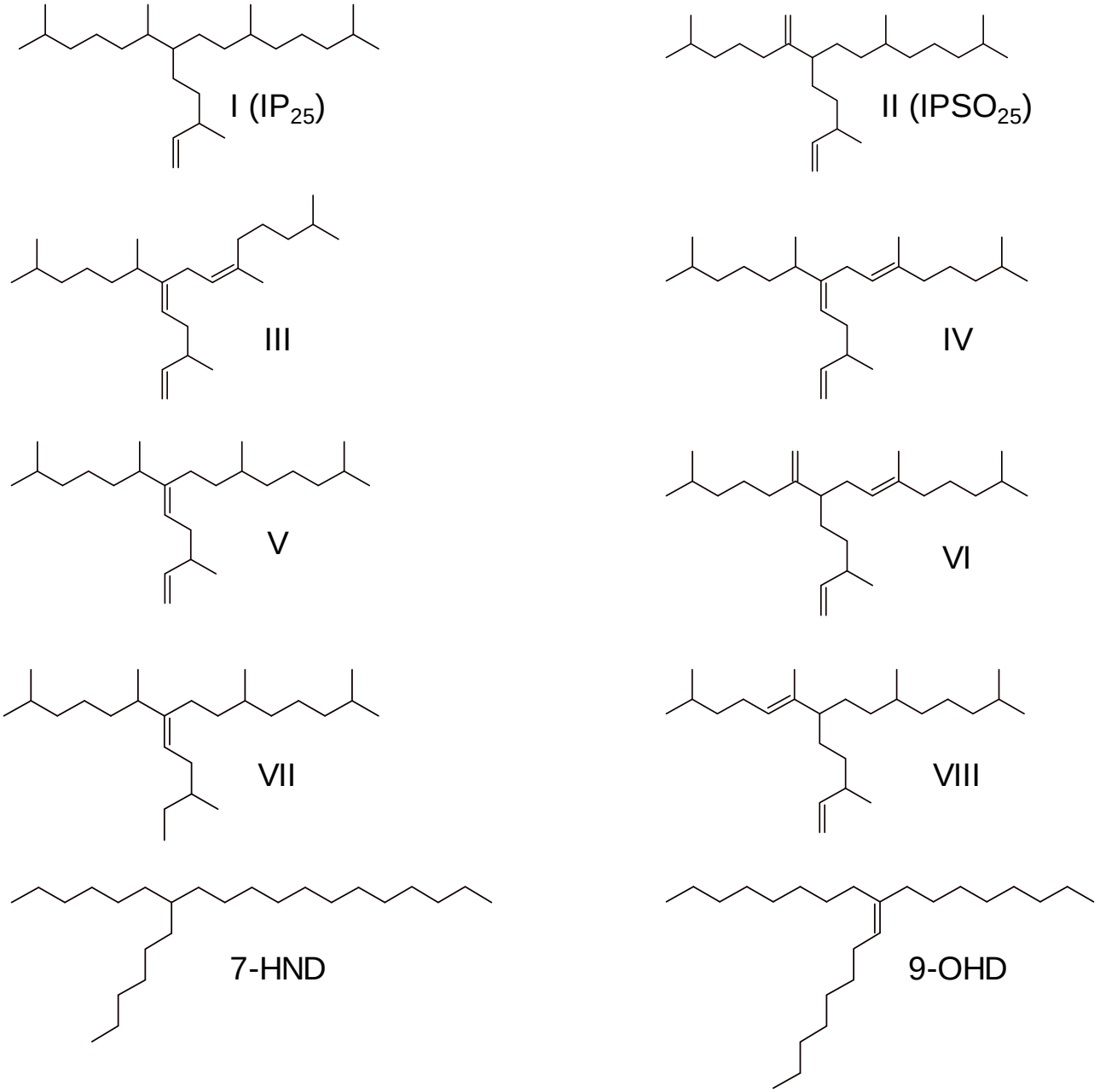
Figure 8. Distributions of $IPSO_{25}$ and HBI III in near surface waters from East Antarctica. Symbol sizes reflect the relative concentration ranges in each case. Note the absence of $IPSO_{25}$ in the Permanently Open Ocean Zone (POOZ). The highest relative abundances of $IPSO_{25}$ and HBI III are found in the Seasonal Sea Ice (SSI) zone and the Marginal Ice Zone (MIZ), respectively, according to the definitions of sea ice conditions used by Smik et al. (2016a). ACC: Antarctic Circumpolar Current; ACoC: Antarctic Coastal Current. Figure adapted from Smik et al. (2016a).

Figure 9. Distributions of IP_{25} and HBI III in surface sediments from the Barents Sea. Symbol sizes reflect the relative concentration ranges in each case. The regions with highest biomarker concentration are also highlighted (red ovals). The white lines indicate the position of the winter (April) sea ice extent: Minimum extent: April 2006; maximum extent: April 1981; median extent: April 1981–2010. The region between the April 1981 and 2006 extent approximates to the MIZ during the spring. Note the highest concentrations of HBI III in the MIZ during spring. In contrast, IP_{25} concentrations are generally highest for locations found

1572 further north where spring sea ice extent is greater; such locations also
1573 experience MIZ conditions during the summer months. Figure adapted from Belt
1574 et al. (2015).
1575
1576 Figure 10. Mass spectra of source-specific HBIs described in the text. Retention
1577 indices are those obtained using an HP5ms GC column. The ion at *m/z* 350 for
1578 $IPSO_{25}$ corresponds to the $(M+2)^{+\cdot}$ ion (see Section 3).
1579
1580 Figure 11: Representative downcore records of IP_{25} and HBI from different
1581 regions of the Barents Sea spanning different timeframes. (a) out-of-phase
1582 profiles reflecting changes in the position of the winter ice margin for annual
1583 advance/retreat cycles; (b) in-phase profiles likely resulting from more rapid
1584 seasonal fluctuations in sea ice dynamics. See the main text (Section 4.1) for a
1585 more detailed discussion. Data taken from Belt et al. (2015), Cabedo-Sanz and
1586 Belt (2016), Stein et al. (2017a) and Kremer et al. (2018b).
1587
1588 Figure 12. Development and application of HBI-based Classification Tree (CT)
1589 models for palaeo Arctic sea ice reconstruction. (a) location of surface sediments
1590 from which HBI distributions were used for CT model construction by Köseoğlu et
1591 al. (2018b). Modern sea ice classifications for each location are also shown; (b)
1592 Outcome of CT model showing the two main predicative variables of sea ice
1593 conditions (i.e. IP_{25} and HBI IV) together with the corresponding threshold criteria
1594 for each sea ice classification; (c) Locations of short cores used to test the CT
1595 model. The four cores represent regions of contrasting modern sea ice extent
1596 (see (a) for colour coding); (d) CT model and PIP_{25}-based estimates of sea ice

conditions for each of the four cores in (c) spanning the last few centuries. Note the agreement between the SpSIC estimates obtained by the PIP_{25} (left-hand axis) and CT model (right-hand axis) approaches. Figures adapted from those in Köseoğlu et al. (2018b). See Section 4.2 and Köseoğlu et al. (2018b) for more detailed discussions.

Figure
Fig.1



Figure

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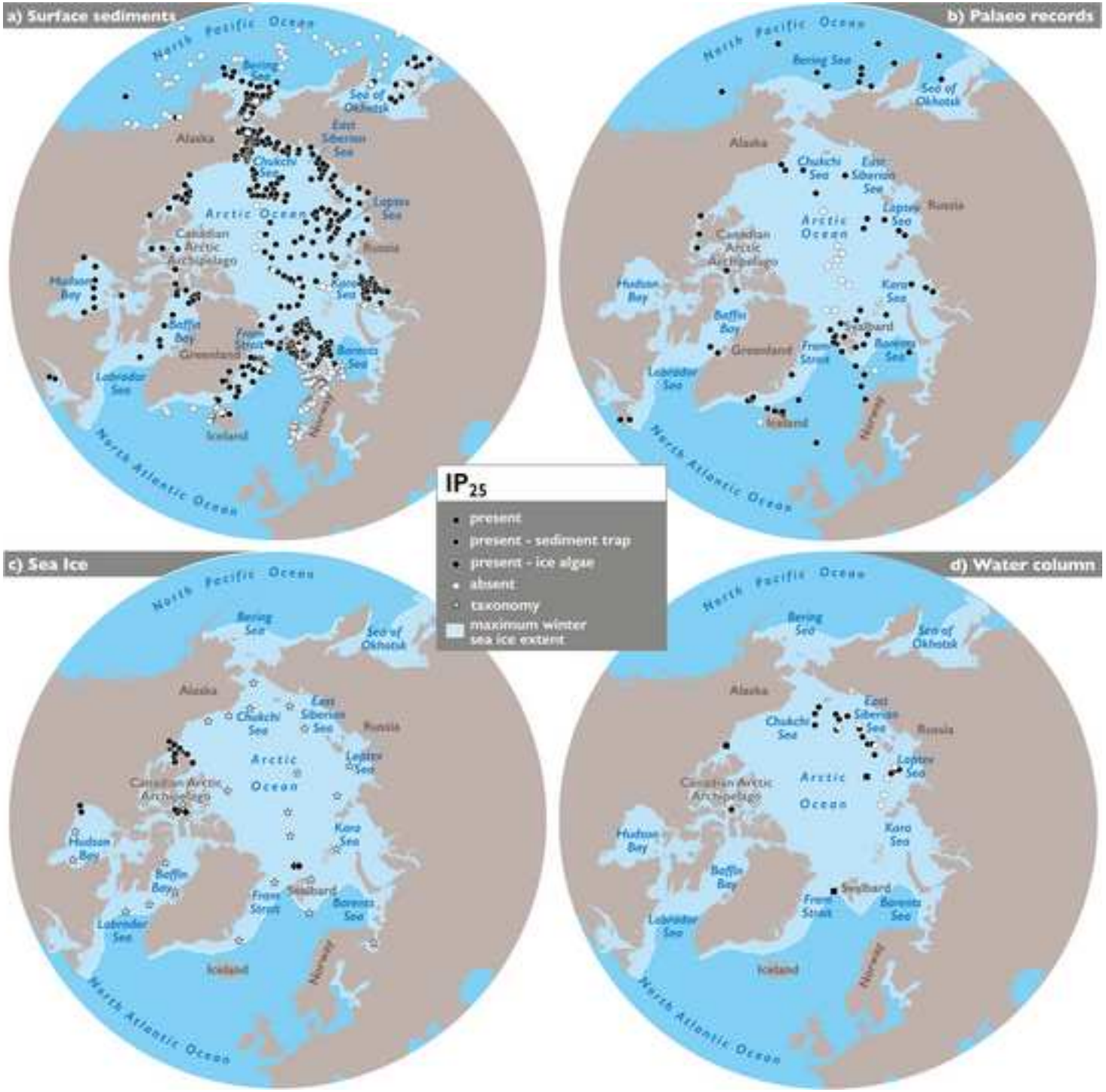
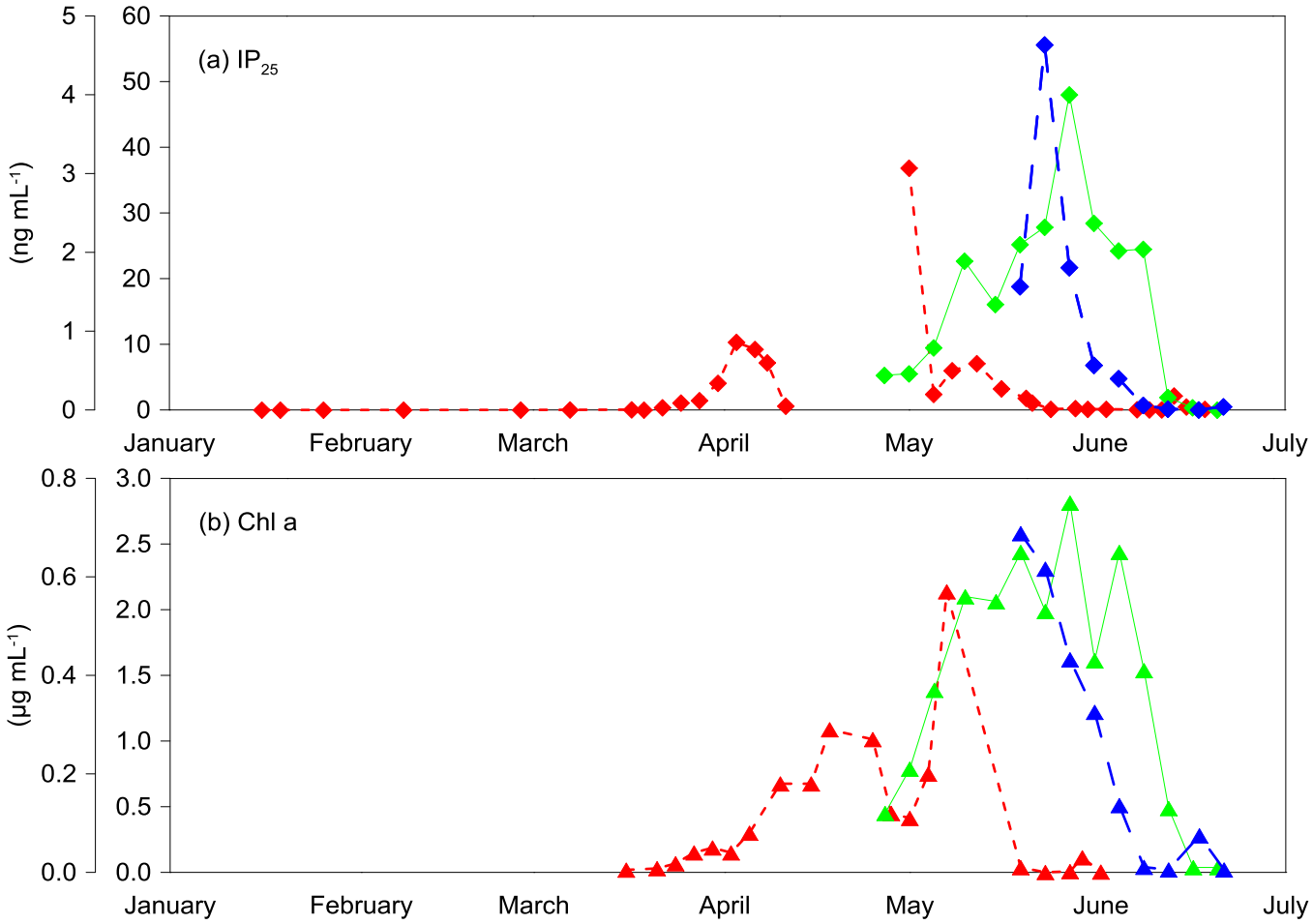
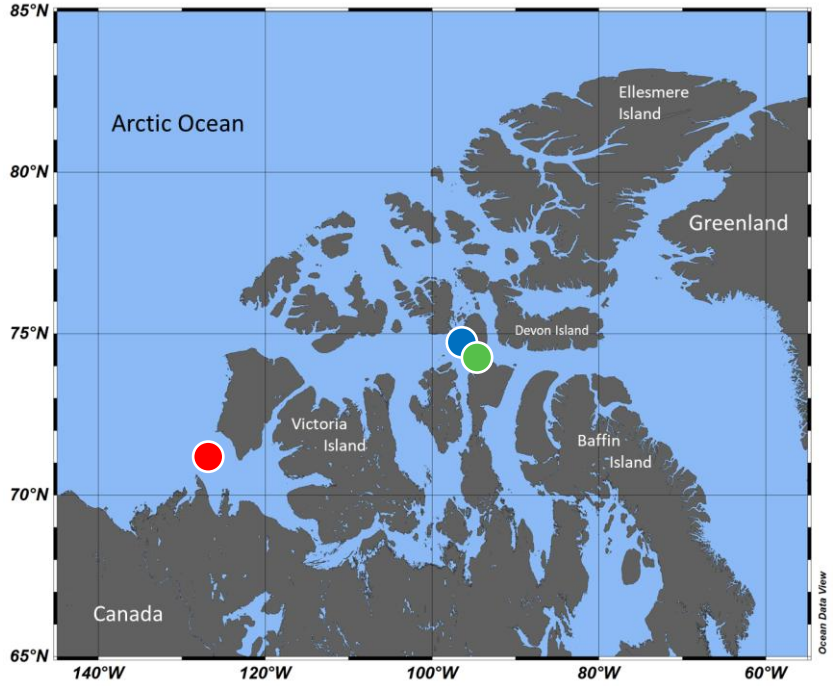


Figure
Fig.3





Figure

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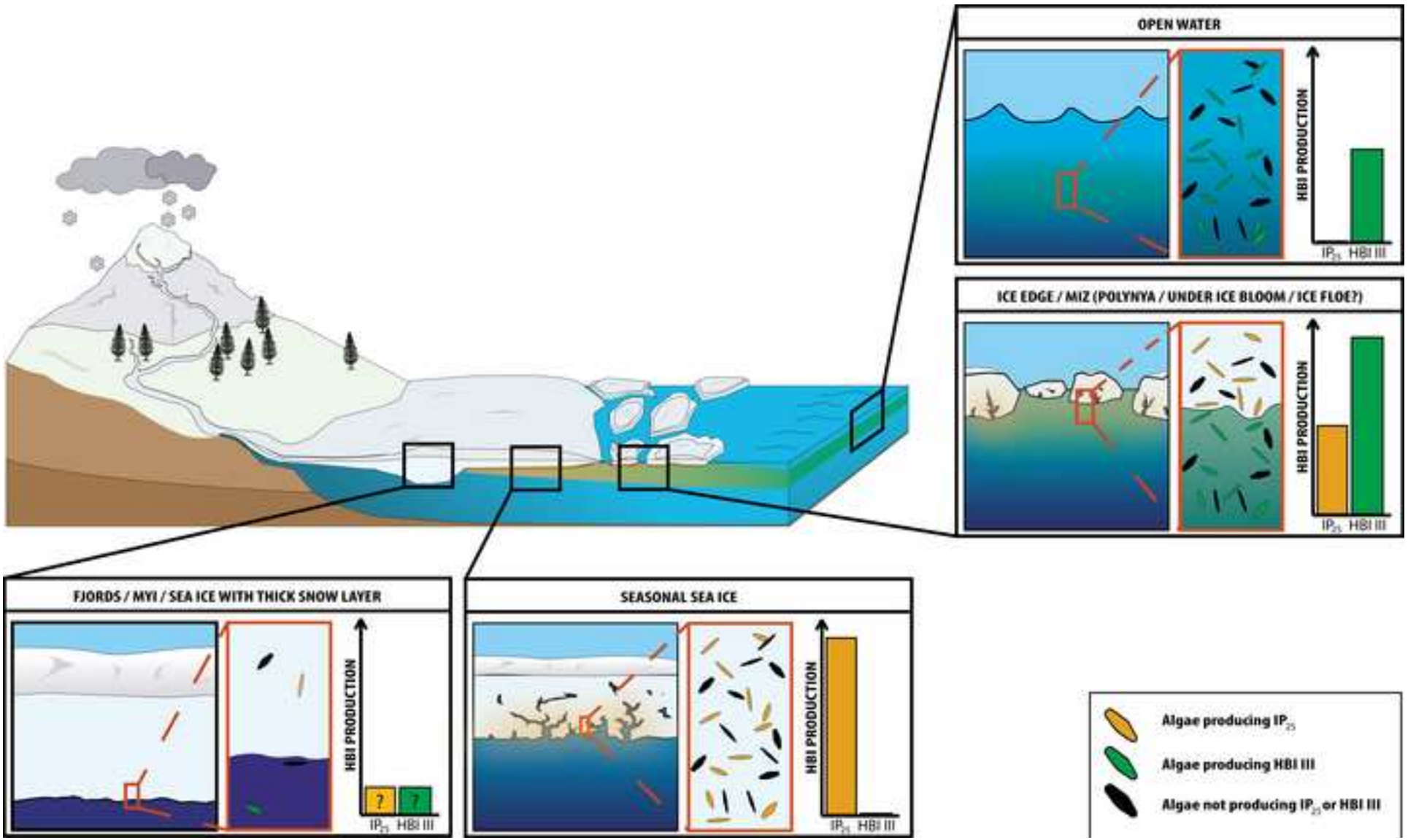

Figure

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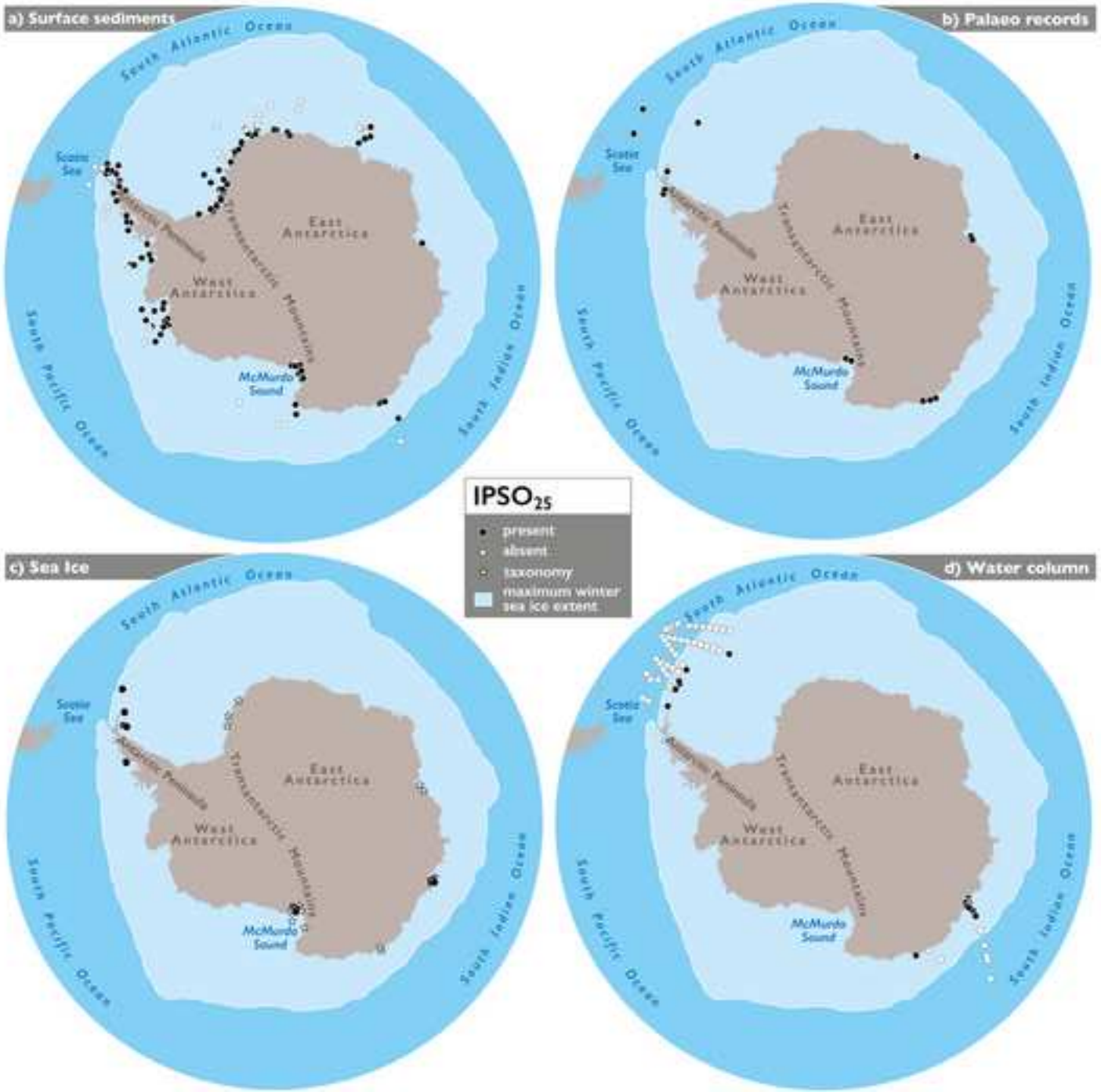
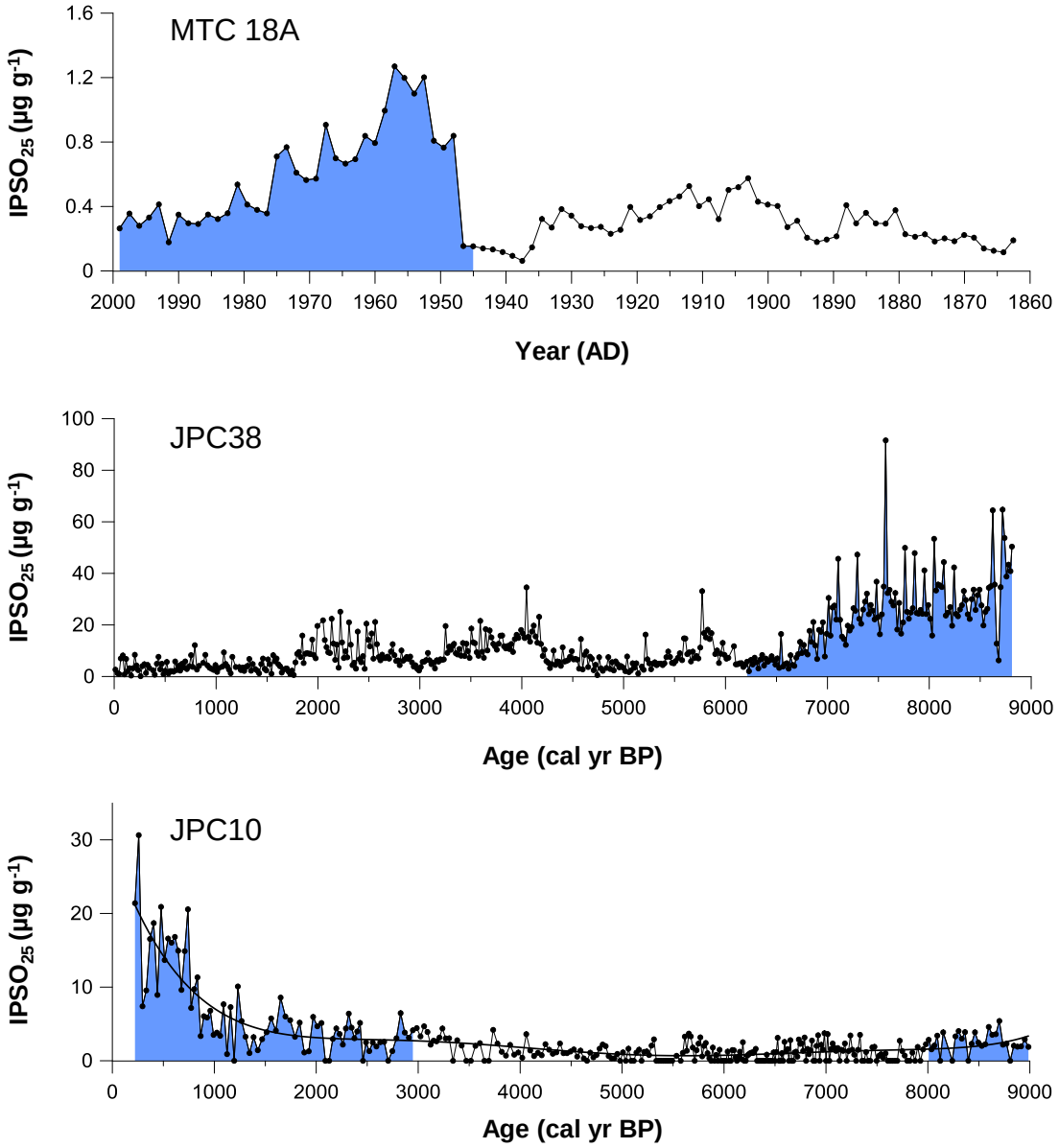
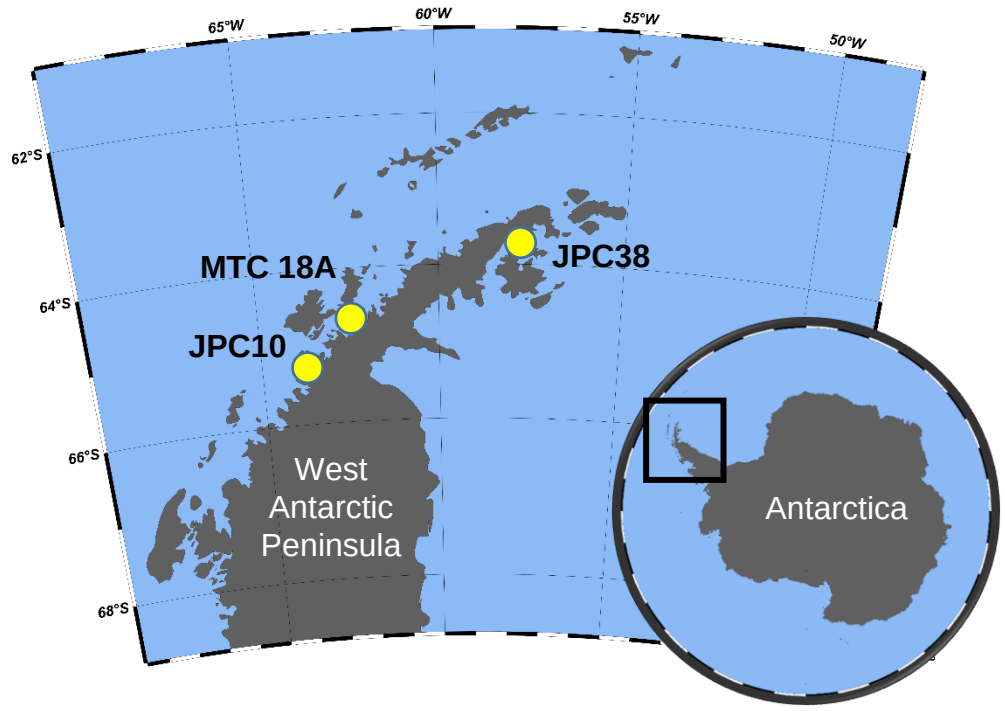


Figure
Fig. 6





Figure

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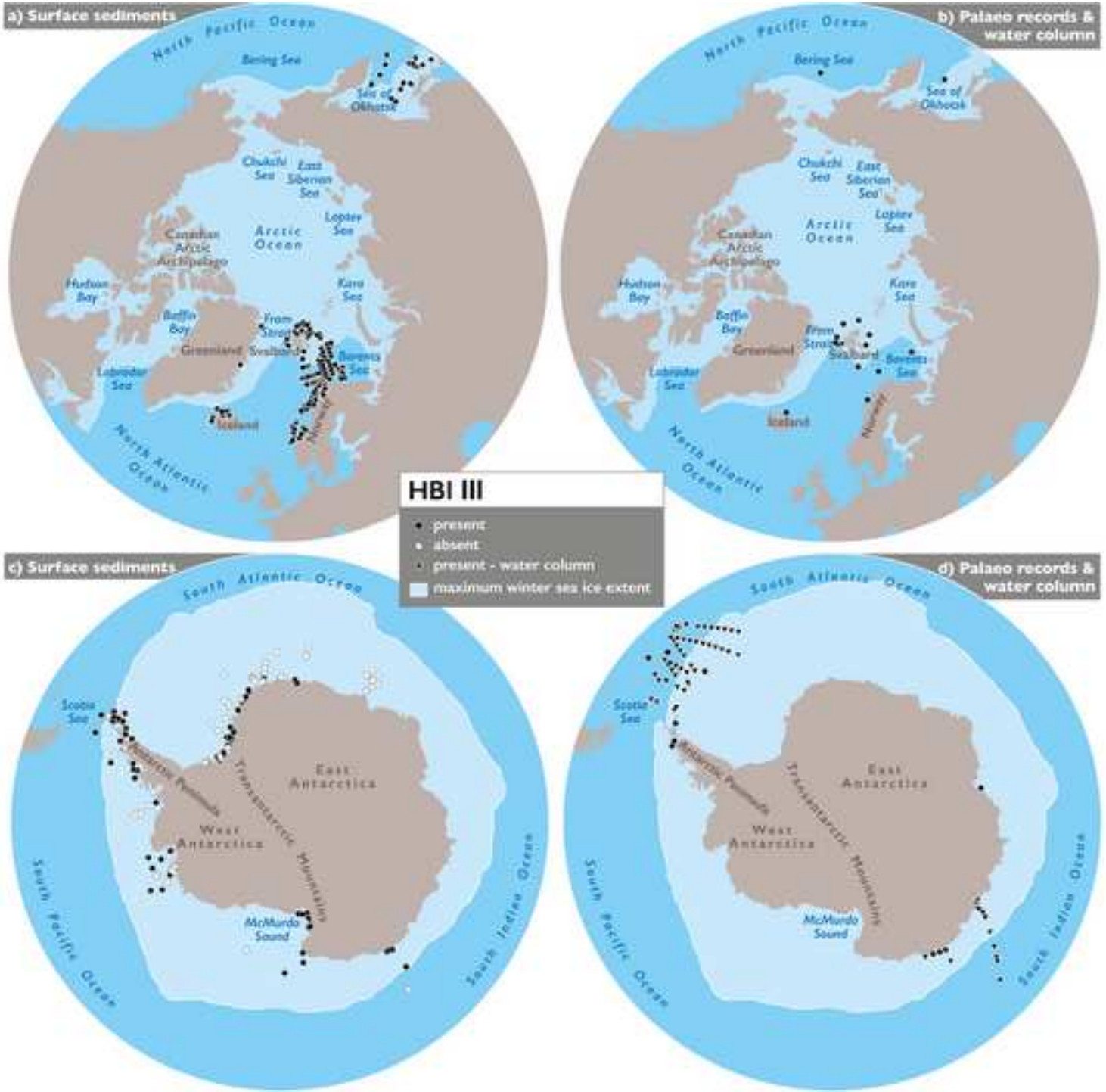
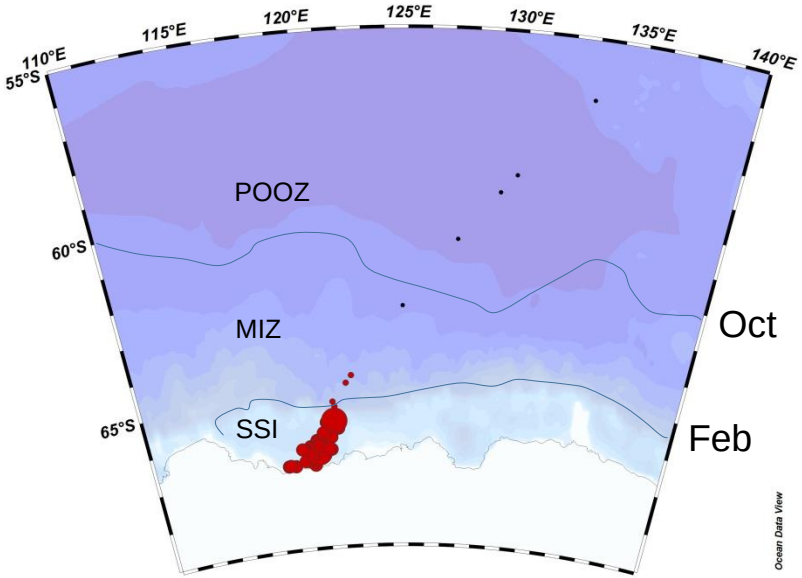
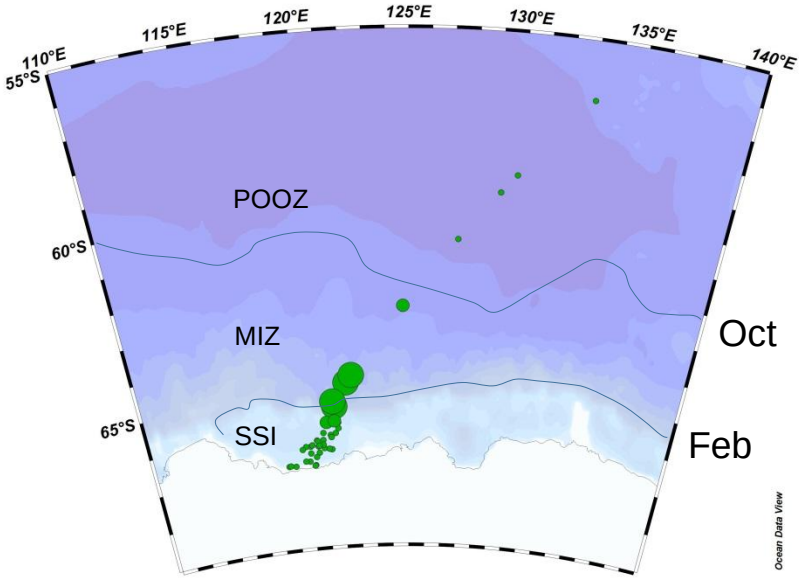


Figure
Fig. 8



$IPSO_{25}$

POOZ	Absent
MIZ	Low
SSI	High



HBI III

POOZ	Low
MIZ	High
SSI	Medium

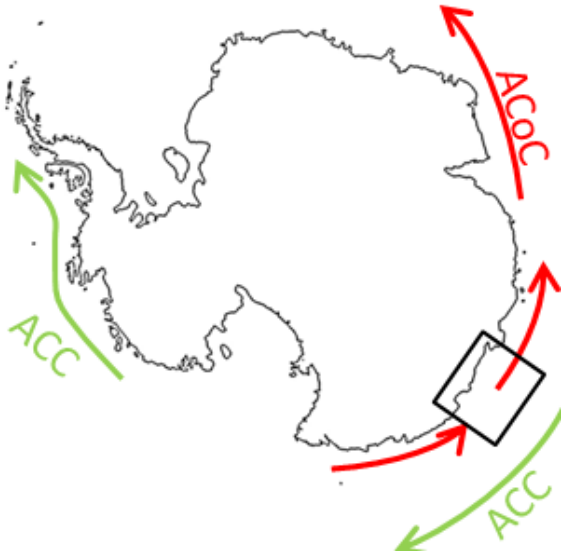


Figure
Fig. 9

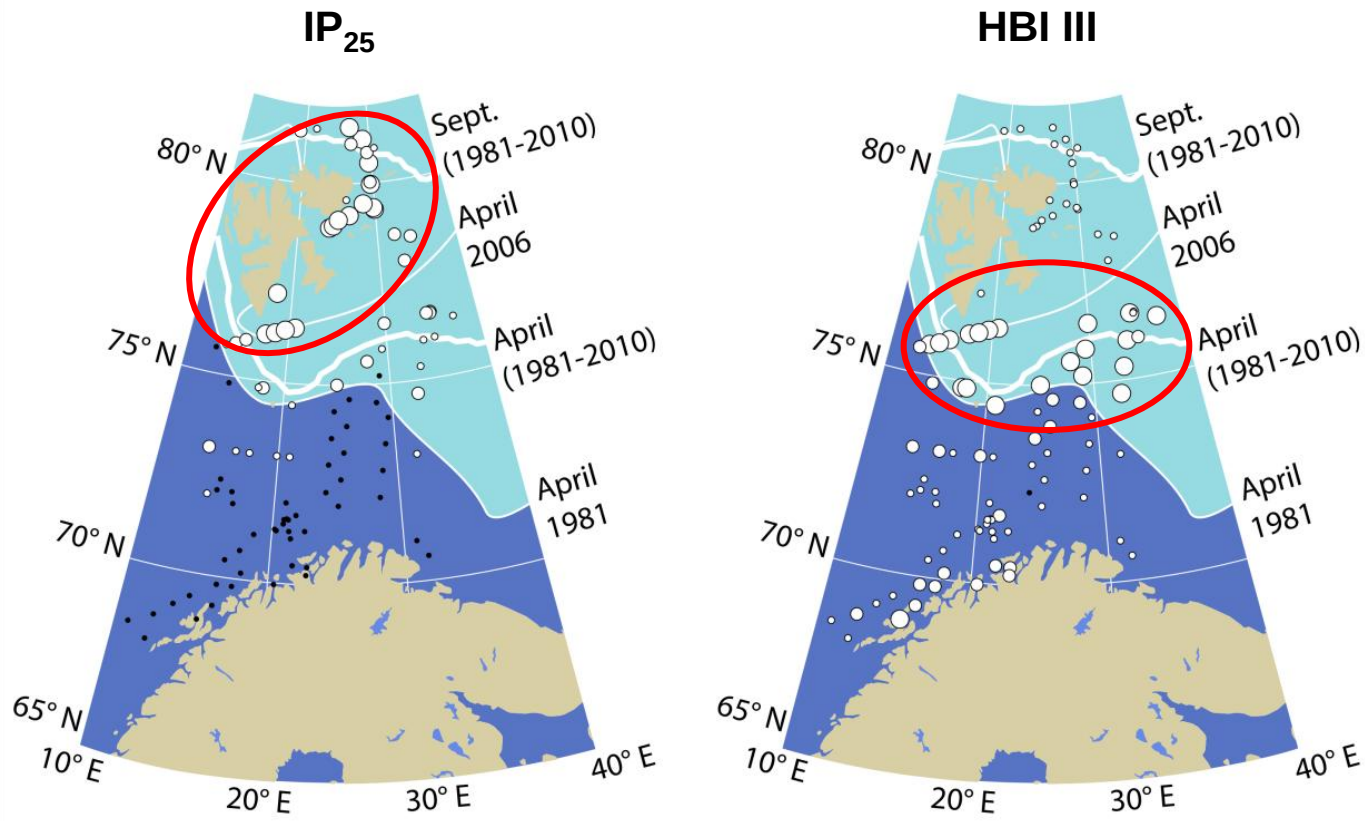
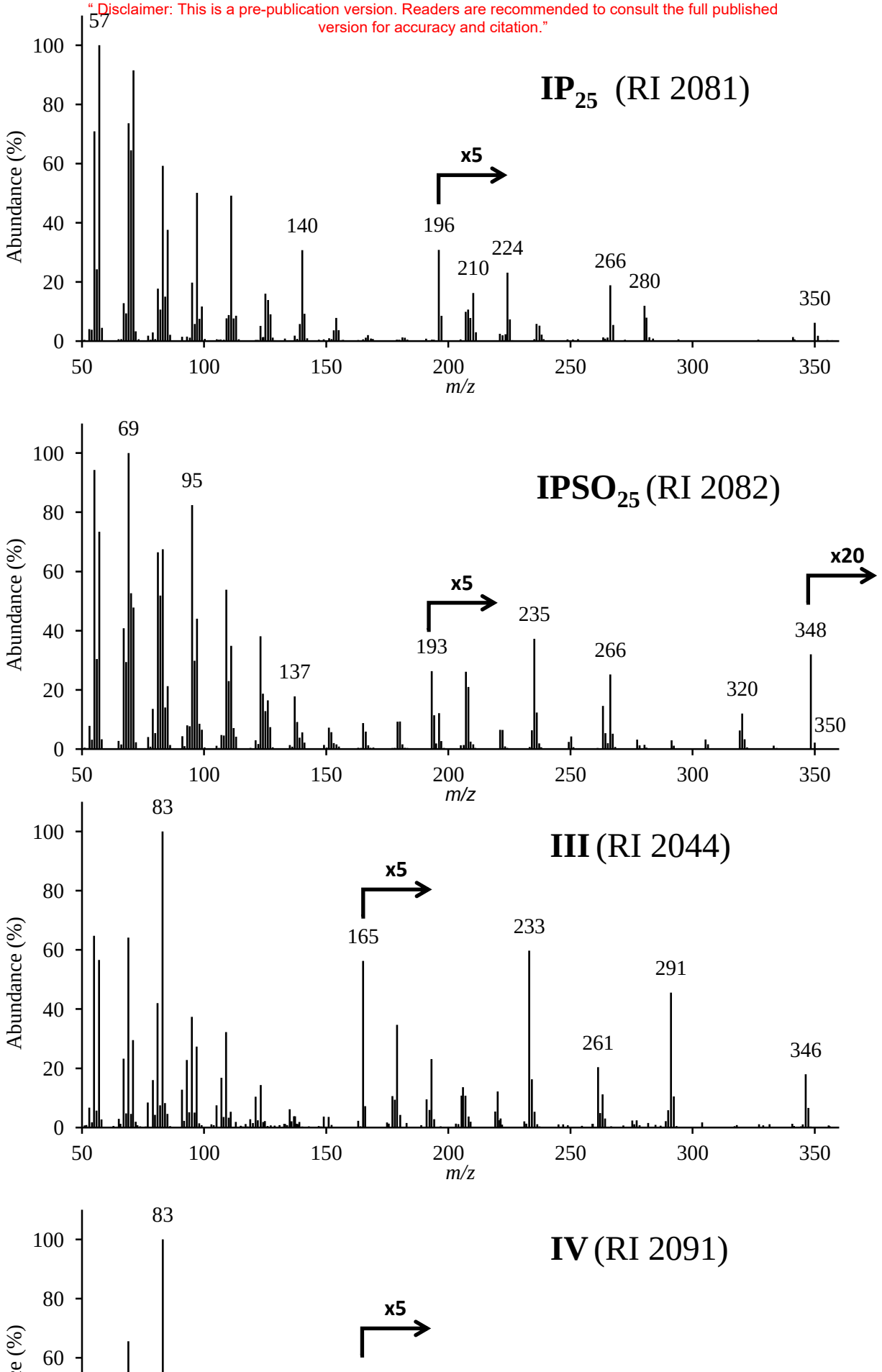
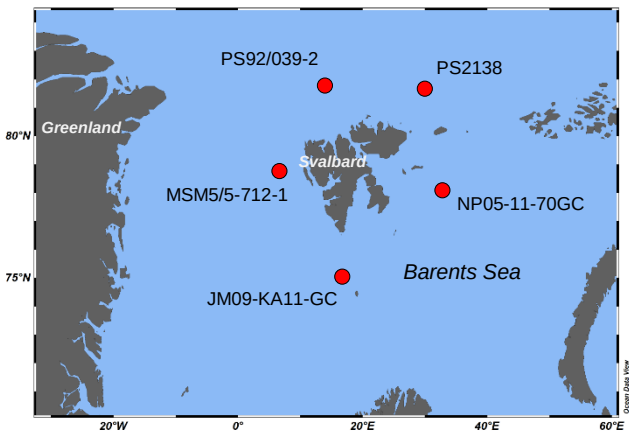


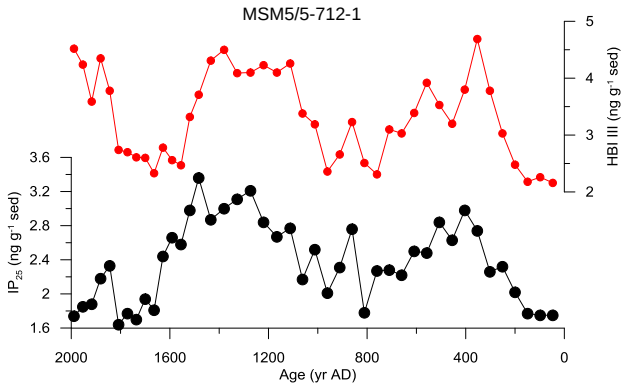
Figure
Fig. 10

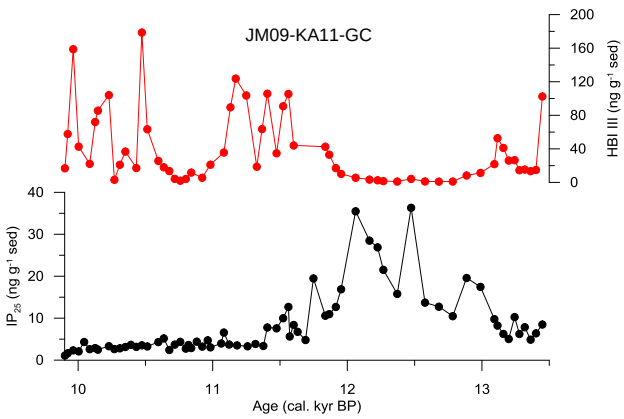


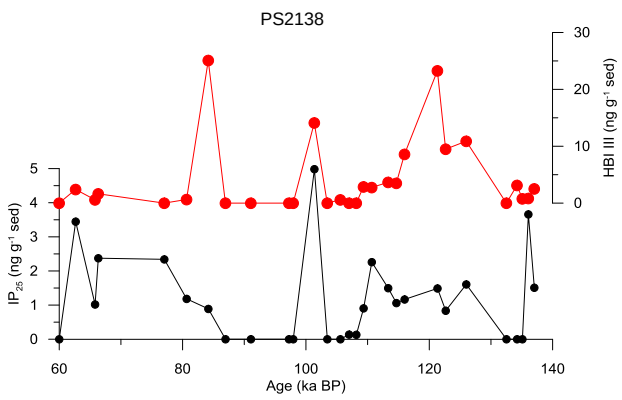
Figure

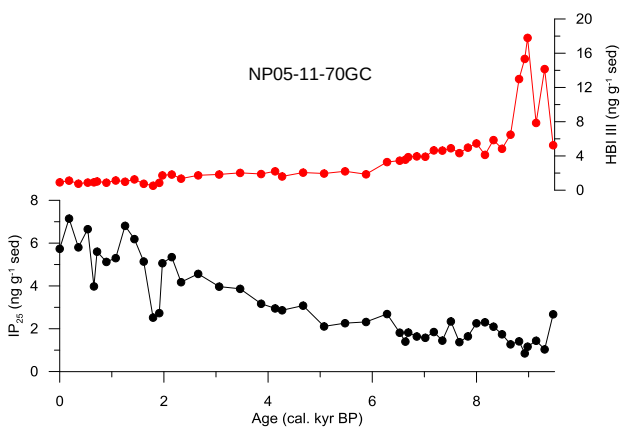
Fig. 11

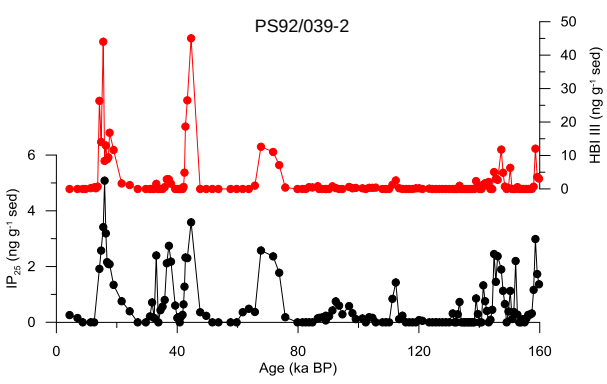








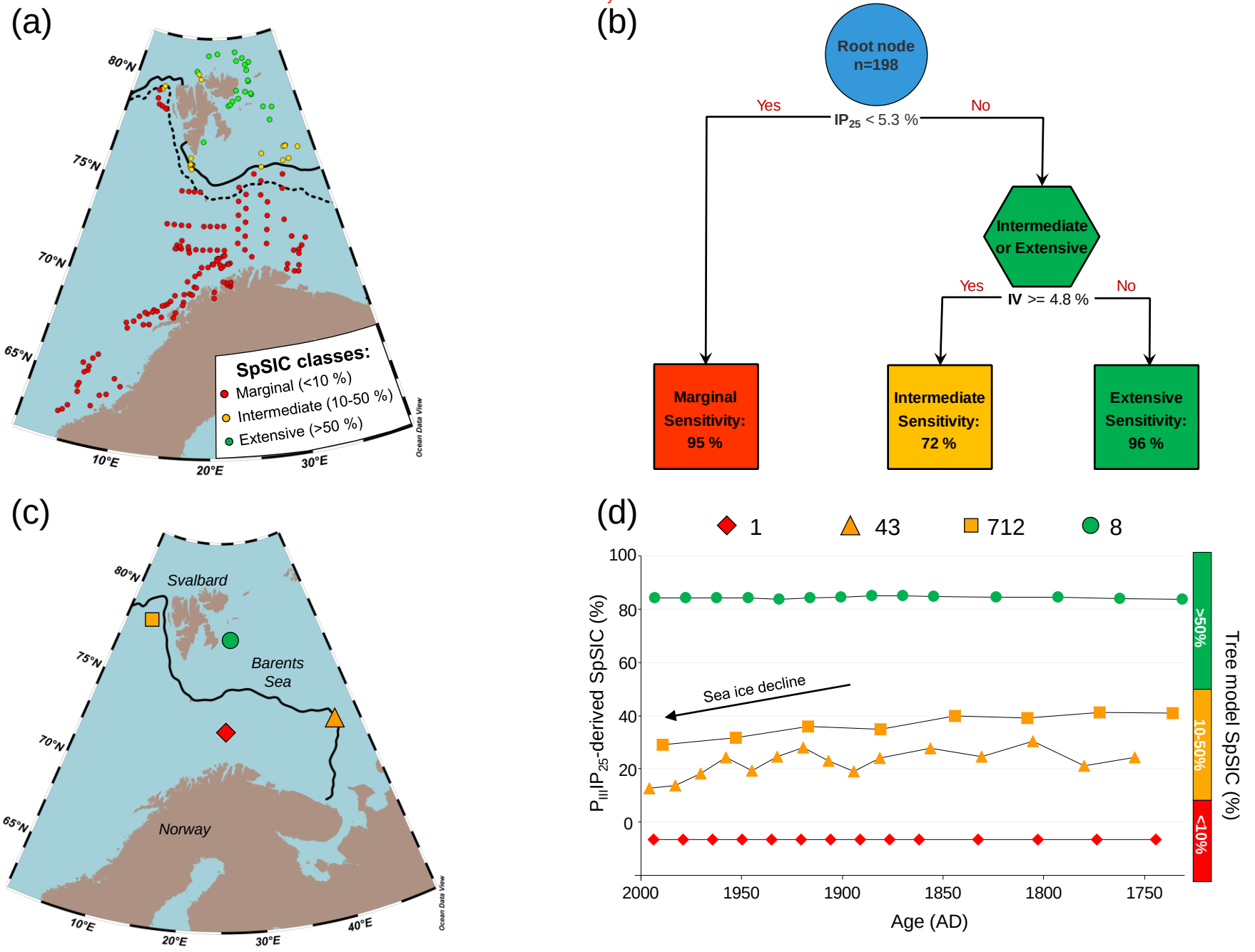




(a) Out-of-phase

(b) In-phase

Figure
Fig. 12



Table

Summary of study locations where source-specific HBIs and other biomarkers have been used in sea ice proxy development studies.

Study region	Sample(s)	Study type	Reference(s)
Arctic			
Arctic Ocean	Sediment traps	IP_{25} (sterols)–seasonal deposition	Fahl and Stein, 2012
	Surface sediments	IP_{25} (PIP_{25})–sea ice calibration	Xiao et al., 2015a
Kara/Laptev Seas	Surface sediments	IP_{25} (PIP_{25})–sea ice calibration	Xiao et al., 2013
			Stoynova et al., 2013
Fram Strait/Svalbard	Sea ice algae	IP_{25} identification	Brown et al., 2017a
	Phytoplankton	Source identification (HBI III)	Belt et al., 2017
	Sediment traps	IP_{25}–seasonal deposition	Lalande et al., 2016
	Surface sediments	IP_{25} (HBI III)–sea ice calibration	Smik and Belt, 2017
		IP_{25} (PIP_{25})-sea ice calibration	Müller et al., 2011
Barents Sea	Surface sediments	CT model development	Köseoğlu et al., 2018b
		$P_{III}IP_{25}$ development	Smik et al., 2016b
		IP_{25} (HBI III)–sea ice calibration	Belt et al., 2015
		IP_{25} (PIP_{25})–sea ice calibration	Navarro-Rodriguez et al., 2013
Norway	Surface sediments	CT model development	Köseoğlu et al., 2018b
Iceland	Surface sediments	IP_{25} (HBI III)–sea ice comparison	Cabedo-Sanz et al., 2016a
	Sediment core	IP_{25}-historical sea ice comparison	Massé et al., 2008
NE/E Greenland	Surface sediments	HBI-sea ice comparison	Ribeiro et al., 2017
			Limoges et al., 2018
		IP_{25} (PIP_{25})–sea ice calibration	Müller et al., 2011
SW Labrador Sea	Sediment cores	IP_{25} (PIP_{25}) vs. other sea ice proxies	Weckström et al., 2013
Baffin Bay	Sediment core	IP_{25} vs. other sea ice proxies	Cormier et al., 2016
	Surface sediments	IP_{25} (PIP_{25})–sea ice calibration	Stoynova et al., 2013
Canadian Arctic Archipelago	Sea ice	IP_{25} identification	Belt et al., 2007
		Sterol identification	Belt et al., 2018
		IP_{25} (sterols)–temporal changes	Belt et al., 2013
			Brown et al., 2011
		IP_{25} (HBI) degradation	Rontani et al., 2014a
	Sea ice algae	IP_{25} source identification	Brown et al., 2014c
	Sea ice/sediment trap/sediments	IP_{25} and HBI II isotopes ($\delta^{13}C$)	Belt et al., 2008
	Water column POM	IP_{25} transfer following ice melt	Brown et al., 2016

Study region	Sample(s)	Study type	Reference(s)
		IP_{25} (HBI) degradation/reactivity	Rontani et al., 2016
	Surface sediments	IP_{25} distribution	Belt et al., 2007,2013
			Tolosa et al., 2013
			Pieńkowski et al., 2017
Hudson Bay	Sea ice	IP_{25} identification	Belt et al., 2007
	Surface sediments	IP_{25} (PIP_{25})–sea ice calibration	Stoynova et al., 2013
		IP_{25} identification	Belt et al., 2007
Bering Sea/Gulf of Alaska	Surface sediments	IP_{25}–sea ice calibration	Sharko, 2010
		IP_{25} (PIP_{25})–sea ice calibration	Stoynova et al., 2013
		IP_{25} (sterols) distribution	Méheust et al., 2013
Sea of Okhotsk	Surface sediments	IP_{25} (PIP_{25})–sea ice calibration	Stoynova et al., 2013
			Lo et al., 2018
Chukchi/E Siberian Seas	Water column POM	IP_{25} distribution	Tesi et al., 2017
	Surface sediments	IP_{25}–sea ice calibration	Sharko, 2010
		IP_{25} (PIP_{25})–sea ice calibration	Stoynova et al., 2013
			Xiao et al., 2015a
Antarctica			
Antarctic Peninsula	Sea ice	Sterol identification	Belt et al., 2018
		$IPSO_{25}$ source identification	Belt et al., 2016
		HBI II ($IPSO_{25}$) identification	Massé et al., 2011
McMurdo Sound	Sea ice	HBI II ($IPSO_{25}$) identification	Nichols et al., 1988,1989,1993
			Johns et al., 1999
E Antarctica	Sea ice	HBI II ($IPSO_{25}$) identification	Massé et al., 2011
	Phytoplankton	HBI II ($IPSO_{25}$) & HBI III distributions*	Smik et al., 2016a
			Massé et al., 2011
	Surface sediments/short cores	HBI II ($IPSO_{25}$) & HBI III distributions*	Massé et al., 2011
	Sediment core	HBI II ($IPSO_{25}$) reactivity*	Sinninghe Damsté et al., 2007
South Atlantic (sub-Antarctic)	Phytoplankton	Source identification (HBI III)	Belt et al., 2017
Scotia Sea	Water column	$IPSO_{25}$ and HBI III distributions	Schmidt et al., 2018
	Sediment cores	$IPSO_{25}$ and HBI III distributions	Collins et al., 2013
Various locations	Surface sediments	$IPSO_{25}$ and HBI III distributions	Belt et al., 2016
			Smik, 2016
Other	Sediments	Analytical method for IP_{25}	Belt et al., 2012b
		Inter-laboraoraty study of IP_{25} (HBIs)	Belt et al., 2014

Study region	Sample(s)	Study type	Reference(s)
	Sediments/extracts	Confirmed structure - sedimentary IP_{25} IP_{25} (HBI) degradation/reactivity	Belt et al., 2012a Rontani et al., 2018a,b Cabedo-Sanz et al., 2016b Belt and Cabedo-Sanz, 2015

* includes some stable isotope ($\delta^{13}C$) data

Table

Summary of study locations and timeframes where source-specific HBIs and other biomarkers have been used for palaeo sea ice reconstructions. For further detail of individual sterols and PIP_{25} indices, please refer to the cited publication(s). *Denotes more than one core.

Study region	Core	Timeframe	Biomarkers	Reference(s)
Arctic				
Arctic Ocean	PS2767-4	Last 60 ka	IP_{25}, HBI II, sterol	Stein and Fahl, 2012
	PS2446-4*	MIS 3-1	IP_{25}, sterol	Xiao et al., 2015b
	PS2138-2	MIS 6-5	IP_{25}, HBI III, sterol, PIP_{25}	Stein et al., 2017a
	PS87/106	Late Miocene	IP_{25}, sterol, PIP_{25}	Stein et al., 2016
Kara Sea	BP00-07/7	Holocene (last 8 ka)	IP_{25}, sterol, PIP_{25}	Hörner et al., 2017
	BP00-36/4*	Last 12 ka	IP_{25}, sterol, PIP_{25}	Hörner et al., 2018
Laptev Sea	PS2458-4	Last 16 ka	IP_{25}, HBI II, sterol, PIP_{25}	Fahl and Stein, 2012
	PS51/154-11*	Last 17 ka	IP_{25}, HBI II, sterol, PIP_{25}	Hörner et al., 2016
Yermak Plateau-Fram Strait	PS92/039-2	Last 160 ka	IP_{25}, HBI III, sterol, PIP_{25}	Kremer et al., 2018b
	ODP Hole 910C	Pliocene/Pleistocene (5.3-2.6 Ma)	IP_{25}, sterol, PIP_{25}	Knies et al., 2014
	ODP Hole 912A*	Quaternary (last 2.2 Ma)	IP_{25}, HBI II–III, sterol, PIP_{25}	Stein and Fahl, 2013
N Svalbard	GeoB10817-4	Ca. 16-8 ka; 2-0 ka	IP_{25}, sterol, PIP_{25}	Bartels et al., 2017
E Fram Strait	MSM5/5-712-1	Holocene (last 2 ka)	IP_{25}, HBI III, sterol, PIP_{25}	Cabedo-Sanz and Belt, 2016
	MSM5/5-723-2*	Holocene (last 9 ka)	IP_{25}, sterol, PIP_{25}	Müller et al., 2012
	MSM5/5-712-2	LGM-Early Holocene (30-9 ka)	IP_{25}, HBI II, sterol, PIP_{25}	Müller and Stein, 2014
	PS2837-5	Last 30 ka	IP_{25}, sterol	Müller et al., 2009
	PS93/006-1	Last 190 ka	IP_{25}, sterol, PIP_{25}	Kremer et al., 2018a
Barents Sea	BASICC 1*	Recent centuries	IP_{25}, HBIs II–VI, PIP_{25}	Köseoğlu et al., 2018b
			IP_{25}	Vare et al., 2010
	JM10-10GC	Mid-late Holocene (last 6.5 ka)	IP_{25}, sterol	Knies et al., 2016
	NP05-11-70GC	Holocene (last 10 ka)	IP_{25}, HBI III, sterol, PIP_{25}	Berben et al., 2017
			IP_{25}, HBIs II–VI, PIP_{25}	Köseoğlu et al., 2018a
	JM09-KA11-GC	Holocene (last 12 ka)	IP_{25}, sterol	Berben et al., 2014
		YD-Holocene (last 13 ka)	IP_{25}, HBI III, sterol, PIP_{25}	Belt et al., 2015
			IP_{25}, HBIs II–VI, PIP_{25}	Köseoğlu et al., 2018a
		LGM (ca. 30-16 ka)	IP_{25}	Knies et al., 2018
N Norway	JM99-1200	YD-early Holocene (13-7 ka)	IP_{25}, HBI III, sterol, PIP_{25}	Belt et al., 2015
			IP_{25}, HBI II, sterol, PIP_{25}	Cabedo-Sanz et al., 2013
			IP_{25}, HBIs II–VI, PIP_{25}	Köseoğlu et al., 2018a
SE Norwegian Sea	JM11-FI-19PC	Last 90 ka	IP_{25}, sterol, PIP_{25}	Hoff et al., 2016
Iceland Sea	ODP 907	Pliocene (3.5–2.4 Ma)	IP_{25}, sterol	Clotten et al., 2018
SW/NE/N Iceland	MD99-2275	Recent millenia	IP_{25}	Massé et al., 2008

Study region	Core	Timeframe	Biomarkers	Reference(s)
			IP_{25}	Axford et al., 2011
	MD99-2263		IP_{25}	Andrews et al., 2009
	MD99-2273		IP_{25}	Sicre et al., 2013
	MD99-2269*	Holocene (last 8 ka)	IP_{25}, HBI III	Cabedo-Sanz et al., 2016a
	MD99-2272	Last 15 ka	IP_{25}, HBI III, sterol, PIP_{25}	Xiao et al., 2017
	B997-326PC1*	Ca. 16-12 ka BP	IP_{25}, HBI II	Andrews et al., 2018
E Greenland	PO175GKC#7*	Recent centuries	IP_{25}, HBI II, sterol	Alonso-García et al., 2013
	PS2641-4	Mid-late Holocene (last 5 ka)	IP_{25}, sterol, PIP_{25}	Kolling et al., 2017
	MD99-2322	Holocene (last 8-9 ka)	IP_{25}	Darby et al., 2017
	PS2641-4		IP_{25}, sterol, PIP_{25}	Müller et al., 2012
W Greenland	HU2008029-12PC	Ca. 17-12 ka BP	IP_{25}	Jennings et al., 2017
		Ca. 26-12 ka BP	IP_{25}, sterol	Jennings et al., 2018
		Last 2.2 ka	IP_{25}, HBI III, sterol, PIP_{25}	Kolling et al., 2018
SW Labrador Sea	A107-04BC*	Recent centuries	IP_{25}, sterol, PIP_{25}	Weckström et al., 2013
	A107-14G	YD-early Holocene (ca. 13-10 ka)	IP_{25}	Pearce et al., 2013,2014
Baffin Bay	2008-029-040BC	Recent centuries	IP_{25}, sterol, PIP_{25}	Cormier et al., 2016
Canadian Arctic Archipelago	99LSSL-001	Recent centuries	IP_{25}, sterol, PIP_{25}	Pieńkowski et al., 2016
	ARC-4*	Holocene (last 7 ka)	IP_{25}	Belt et al., 2010
	ARC-3	Holocene (last 10 ka)	IP_{25}, HBI II	Vare et al., 2009
Bering Sea	BR07	Holocene (ca. 11–2 ka)	IP_{25}, HBI II, sterol, PIP_{25}	Ruan et al., 2017
	SO201-2-12KL*	Last 18 ka	IP_{25}	Méheust et al., 2016
	SO202-07-6*	LGM-Holocene (ca. 25–5 ka)	IP_{25}, sterol, PIP_{25}	Méheust et al., 2018
	LV29-114-3*	Ca. 138–70 ka BP	IP_{25}	Max et al., 2014
	U1343	MPT (ca. 1.53–0.34 Ma)	IP_{25}, HBI III	Detlef et al., 2018
Sea of Okhotsk	MD01-2414	Last 130 ka	IP_{25}, HBI III	Lo et al., 2018
Chukchi-Alaskan Margin	HLY0501-05TC/JPC*	Holocene (last 11 ka)	IP_{25}, sterol, PIP_{25}	Polyak et al., 2016
Chukchi/E Siberian Seas	ARA2B-1A*	Holocene (last 10 ka)	IP_{25}, sterol, PIP_{25}	Stein et al., 2017b
Antarctica				
Western Antarctic Peninsula	JPC-10	Holocene (last 9 ka)	HBI II ($IPSO_{25}$), HBI III	Etourneau et al., 2013
Antarctic Peninsula	MTC-38C*	Recent centuries	HBI II ($IPSO_{25}$), HBI III	Barbara et al., 2013
	JPC-38	Holocene (last 9 ka)	HBI II ($IPSO_{25}$), HBI III	Barbara et al., 2016
E Antarctica	MD130-MC02	Recent seasons	HBI II ($IPSO_{25}$), HBI III	Massé et al., 2011
	DTCI2010	Recent decades	HBI II ($IPSO_{25}$), HBI III	Campagne et al., 2016
	CB2010	Recent centuries	HBI II ($IPSO_{25}$), HBI III	Campagne et al., 2015
	SMB-Ellis Fjord		HBI II ($IPSO_{25}$)	Sinninghe Damsté et al., 2007
	MD03-2601*	Holocene (last 9 ka)	HBI II ($IPSO_{25}$), HBI III	Denis et al., 2010
	NBP0101-JPC24	Deglaciation (11–9 ka)	HBI II ($IPSO_{25}$), HBI III	Barbara et al., 2010

Study region	Core	Timeframe	Biomarkers	Reference(s)
Scotia Sea	TPC286*	Last 60 ka	HBI II ($IPSO_{25}$), HBI III	Collins et al., 2013
McMurdo Sound (Ross Sea)	83-3a	Unspecified (short core)	HBI II	Venkatasen, 1988
Lützow-Holm Bay	Core A*	Unspecified (short core)	HBI II	Matsumoto et al., 1992